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Atmospheric
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Discussions

# *Interactive comment on* "Energetic particle precipitation in ECHAM5/MESSy – Part 2: Solar Proton Events" *by* A. J. G. Baumgaertner et al.

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We would like to thank the referee for his valuable comments, which we address below.

The only general comment by the referee concerns the N/NO production parameterisation as he misses a clear scientific justification. For EMAC as with most other models (as found during the HEPPA SPE initiative led by Bernd Funke, a paper summarizing these results is in preparation), there is a strong disagreement for $N_2O$ after solar proton events, while the $NO_y$ chemistry normally produces reasonable results for the middle atmosphere. While Funke et al. (2008) were able to diminish these differences by adding a branch to the reaction of ground state atomic nitrogen with $NO_2$, this modification did not achieve the same effect for the EMAC model.

We present an alternative approach to reconcile the observed $N_2O$ concentrations by adjusting the N/NO production ratio. We have chosen this branching ratio as tuning parameter because neither experiments nor theoretical studies have provided accurate values by now. Values ranging from 0.33 to 2.5 for the total production of N and NO have been reported in previous work. Thus, its adjustment by means of a fit to MIPAS data is appropriate as long as the resulting branching ratio does not significantly exceed the spread of values reported in the literature. It should be noted, however, that we do not aim at providing a scientific justification for modification of this parameter (which would be beyond the scope of this paper) but at identifying potential error sources responsible for the model/data mismatch and - in this sense - to motivate future experimental studies.

The method presented in the manuscript used to reconcile $N_2O$ concentrations appears to be a manifest approach because the 0.55 $N(^4S)$ / 0.7 NO branching ratio commonly used has only been derived by “best fit” between models and observations in the past. We support this statement with the following discussion of the involved processes and of previous studies on this subject.

Impacting protons with energies from 100 keV to 1 GeV that reach the mesosphere or stratosphere are too energetic to be efficient in dissociating nitrogen (Crutzen et al., 1975), but deposit their energy in the accessible states of $N_2$ and $O_2$ by secondary electrons of low energy (<100eV), see Porter et al. (1976). These act on $N_2$ and $O_2$ to initially produce N, $N^+$, $N_2^+$, O, $O^+$, and $O_2^+$; for details on these reactions see e.g. Rusch et al. (1981). Further reactions lead to the production of $N(^4S)$, $N(^2D)$, and $N^+$ (which via reaction with $O_2$ also reacts further to $N(^2D)$) as well as other electronically excited states of N and O probably of less importance (for nitrogen: $N(^2P)$, $N(3s^2P)$, $N(3s^4P)$, $N(3s^2D)$, $N(4s^2P)$). Note that several of the involved reaction rates and branching ratios have not been experimentally determined (Rusch et al., 1981). The following reactions then lead to the formation of NO:

$$\mathrm{N(^4S) + O_2 \rightarrow NO + O} \tag{R1}$$

$$\mathrm{N(^2D) + O_2 \rightarrow NO + O.} \tag{R2}$$

Reaction (R1) is slow and highly temperature dependent, while reaction (R2) is fast and thus the main source for NO.

Additionally, $N(^2D)$ can react with O or NO:

$$\mathrm{N(^2D) + O \rightarrow N(^4S) + O} \tag{R3}$$

$$\mathrm{N(^2D) + NO \rightarrow N_2 + O.} \tag{R4}$$

Additional to the reaction (R1), $N(^4S)$ also takes part in the following reactions:

$$\mathrm{N(^4S) + NO \rightarrow N_2 + O} \tag{R5}$$

$$\mathrm{N(^4S) + NO_2 \rightarrow N_2O + O.} \tag{R6}$$

Many atmospheric chemistry models do not include ion or detailed excited state chemistry, so in order to parameterise solar proton events, the formation of ground state N and NO is required as a function of ionization rate. However, because of reactions (R5) and (R6) it is not possible to assume an NO production rate normalized to the ionization rate, as pointed out e.g. by Rusch et al. (1981). We would also like to point out that the branching ratio $N(^4S)/N(^2D)$ is not necessarily equal to the ratio $N(^4S)/NO$ because of the additional reactions listed above.

Crutzen et al. (1975) mentioned that from the experimental studies of Winters (1966), Rapp et al. (1965), and Rapp and Englander-Golden (1965) a rate of production of 1.5 N atoms per ion pair can be estimated. However, the ratio N($^4$S)/N($^2$D) or N($^4$S)/NO was not determined. Porter et al. (1976) write that additional studies concerning atomic nitrogen production were limited to high energy secondary electrons ($>$ 100 keV) and are thus not applicable for SPEs. The work of Porter et al. (1976) is the only theoretical study that used an atomic cross section approach to derive a production of 1.27 atoms per ion pair for proton impact at 1 MeV, distributed over 8 different states including $N^+$ (see their Table V). While the ratio of N($^4$S)/N($^2$D) can be deduced from this, it is not possible to accurately derive the N/NO production ratio. It is also interesting to note that Porter et al. (1976) found that, "it is observed that the efficiency for production of atomic species changes with the particle energy", which effectively means that such production at least for proton energies below 1 MeV is height dependent since the particle energy determines the height it reaches.

As discussed in the following, newer SPE studies generally base their branching ratios either on approximations to Porter et al. (1976), often assuming that the ratio N($^4$S)/NO ratio is equal or similar to the N($^4$S)/N($^2$D) ratio, or derive such branching ratios by fitting their model results to observations. A review article by Jackman and McPeters (2004) states "Estimates of the number of $NO_y$ constituents created per ion pair range from 0.33 (Warneck, 1972) up to 2.5 (Fabian et al., 1979). Recent publications show only small differences and range from 1.25 (Jackman et al. 1990) up to 1.3 (Reid et al., 1991) $NO_y$ constituents produced per ion pair." The study by Fabian et al. (1979) based their assumption on rocket measurements of mesospheric and thermospheric NO concentrations as well as ionisation rates. The work by Warneck (1972) is a modeling study based on production rates of 0.64 for $N_2^+$ and 0.16 for $N^+$ as published by Dalgarno (1967). However, Dalgarno (1967) derived from the initial $N_2^+$ and $N^+$ creation a production of 0.8 N and 0.5 NO "with a possible doubling of [the production rate of] NO at night", which is in disagreement with the 0.33 $NO_y$ constituents derived by Warneck (1972). Reid et al. (1991) indeed use a value of 1.3 $NO_y$ molecules per ion pair: “Following Rusch et al, 1981, we assume that 1.3 $NO_y$ molecules are produced per ion pair, partitioned between the ground $N(^4S)$ state and exited states (mainly 2D) at 20 and 80%.” The Rusch et al. (1981) paper is a theoretical study that includes a comparison of model results and observations, however, they base their results on several assumptions that were not experimentally verified, and their conclusions are also build on “best fit” to observations: “A production of 1.3 odd nitrogens per ion par, an 80% branching ratio for the production of $N(^2D)$ by the primary reactions dissociating $N_2$, and inclusion of the loss of $NO_x$ through N+NO in a time-dependent calculation appears to produce an ozone destruction most compatible with the measurements.” The other study cited in Jackman and McPeters (2004) is Jackman et al. (1990). They state “This calculation assumed 1.25 nitrogen (N) atoms produced per ion pair which is similar to the value given by Porter et al. (1976), derived using a detailed theoretical energy degradation computation. The agreement between the predicted and measured NO increase following the July 1982 SPE has given us confidence in the reliability of the computations for $NO_y$ species increase caused by SPEs. We therefore assume that 1.25 N atoms are produced per ion pair for all base model computations in this paper.”

The N/NO branching is discussed in a newer modeling study by Jackman et al. (2005) who state “In order to best represent the production of $NO_y$ constituents by the protons and their associated secondary electrons, we assume that 45% of the N atoms produced per ion pair result in the production of $N(^4S)$ ($\sim$0.55 per ion pair) and that 55% of the N atoms produced per ion pair result in the production of NO ($\sim$0.7 per ion pair).” It appears that this choice is also based on a best fit to observations of $NO_y$.

We conclude, that established $N(^4S)$/NO ratios are not firmly supported by theoretical or experimental work or are inconsistent.

We have included this discussion in the revised manuscript.

Replies to detailed comments:

**Page 4507, lines 3-8** The bulk of ionization occurred on 29 October, therefore comparing the averages for that day is sufficient for the 2003 Halloween event. We agree that the differences should be quantified and we have revised the relevant section as follows: “Although there is general agreement, the vertically integrated ionization rate averages for 29 October differ by 16%. In particular, the ionization rate altitude dependence is not satisfactory; at 45 km on 29 October for example an overestimation of approximately 50% is found. However, a correct altitude dependence is crucial due to the steep profiles of ozone and other constituents that the SPE affects. Therefore, a series of sensitivity studies was performed using different sets of a and b in Eq. 1. Values for a between 9 and 14, for b between 1 and 3 were tested. Using a = 12.3 and b = 1.8 yield the best agreement between the calculated and published ionization rates reducing the difference between the vertically integrated rates to 5%. The results are shown as the red lines in Fig. 1.“

**Page 4508, lines 6-7** The paragraph was extended with the following statement on the differences as requested: “The box model does not contain heterogeneous chemistry, and the radiation environment (for photolysis) is different in that a climatological ozone profile is assumed.”

**Page 4508, lines 16-17** The relevant paragraph was amended by the following statement: “The differences between the employed baseline versions are small and generally simply cover different days of the concerned period.“

**Fig 4 et al** All Figures use day and night data. We agree that the SPE effect varies diurnally, however, the input data and the submodel are not capable of a realistic capture of such short-term effects. Therefore, we focus on the effects after the SPE. We have clarified this in the section on the MIPAS data: “No restrictions were made with respect to solar zenith angle limits and both day and night data were used." and in the results section: "Note that day and night data were used to create this figure and similar figures below."

**page 4509, lines 8-9** This statement refers to the comparison with Fig. 3 of Jackman et al. (2005). Unfortunately we do not have access to the data that was used to create this Figure, so a quantitative comparison is not possible. Therefore, we have to base this statement on a visual comparison of the contour lines. We have weakened this statement: "There appears to be a very good agreement with the ionization rates calculated by ..."

**Page 4509, line 14-15** We have indicated the relaxation e-folding times in section 2: "Results from setups that were nudged as well as from free-running setups will be shown here. Nudging was applied between levels 18 ($\sim$1.5 hPa) and 84 ($\sim$715 hPa) with relaxation e-folding times of 12 h for temperature, 6 h for vorticity, 48 h for divergence and 12 h for surface pressure. Below (down to level 13 or $\sim$0.7 hPa) and above (up to level 87 or âĹij920 hPa) these levels stepwise reduced coefficients were applied."

**Page 4510, lines 6-7** The text was revised as follows: During the SPE, MIPAS shows lower mesospheric enhancements up to 50 ppbv where the model reaches 60 ppbv. During the initial phase of the SPE the $NO_x$ enhancements are centered around the geomagnetic pole, then gradually transported and mixed to other areas including lower latitudes (not shown). This leads to large sampling errors (see Sect. 3) and standard errors; the standard error for $NO_2$ at 55 km for the area 70°N–90° N is 13 ppbv calculated from 69 MIPAS profiles. In the light of these aspects, the agreement between EMAC and MIPAS is acceptable. Higher up the model overestimates the enhancements by up to 100%. In the following weeks downward transport of the enhancements can be seen in both the model results and the measurements. Note that the enhancements in the MIPAS data in the upper mesosphere during the second half of November are not related to in-situ production of $NO_x$ but originate in the lower thermosphere and are transported downward. This effect is not subject of the work presented here, but is discussed in the companion paper by Baumgaertner et al. (2009). Also note that on 6 and 7 November only 5 profiles were obtained by MIPAS in this area, with an ensemble mean precision of 1.5 ppbv and standard error of 21 ppbv at 50 km. Similarly, on 12 and 13 November only 6 profiles were obtained, with an ensemble mean precision of 1.0 ppbv and a standard error of 11 ppbv. Therefore the enhancements during both these periods are probably not representative for the full polar cap, given that flux measurements did not show any anomalies during these times.

**MIPAS observations** We have added the following to the description of the MIPAS data: “Here, we use the retrievals performed with the IMK-IAA data processor and the Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA), which were also used in the aforementioned MIPAS studies.”

We also added information on errors, vertical resolution, and altitude coverage: The MIPAS measurement errors and vertical resolution for a single profile are listed in Table  for 40 km and 60 km altitude. Note that if an ensemble of measurements is considered, the precision of the mean (also termed random error) is reduced by a factor equal to the square root of the number of measurements. The systematic error and the vertical resolution do not change with the number of measurements. Additionally, the standard error of an ensemble mean needs to be considered, which accounts for natural variability as well as measurement precision. During highly disturbed conditions, such as for $NO_2$ during the initial phase of an SPE, the standard error can be much larger than the precision. The sampling error, i.e. the error related to the fact that only a limited number of measurement points in time and space of a “true distribution” exist, has not been quantified.

**Page 4510, lines 14-15** The paragraph was revised as follows: “The measurements

| | Single profile precision for 70–90°N; given in vmr and percent under quiet and disturbed (in brackets, 30 Oct – 5 Nov) conditions | | Systematic error | | Vertical resolution (km) for 70–90° N | |
|---|---|---|---|---|---|---|
| | 40 km | 60 km | 40 km | 60 km | 40 km | 60 km |
| $O_3$ | 0.26 ppmv / 6(6)% | 0.11 ppmv / 10(14)% | 0.33 ppmv | 0.0067 ppmv | 4 | 9 |
| $HNO_3$ | 0.15 ppbv / 9(7)% | 0.37 ppbv / 42(22)% | 0.30 ppbv | 0.32 ppbv | 8 | 43 |
| $N_2O_5$ | 0.18 ppbv / 18(40)% | 0.041 ppbv / 54(90)% | 0.064 ppbv | 0.0081 ppbv | 7 | 52 |
| $N_2O$ | 0.63 ppbv / 45(67)% | 0.46 ppbv / 26(15)% | 0.027 ppbv | 0.45 ppbv | 4 | 13 |
| $NO_2$ | 1.7 ppbv / 11(13)% | 4.6 ppbv / 9(10)% | 0.86 ppbv | 5.1 ppbv | 7 | 13 |
| HOCl | 0.12 ppbv / 63(44)% | 0.0019 ppbv / 70(50)% | 0.0013 ppbv | 0.000049 ppbv | 15 | 17 |
| $ClONO_2$ | 0.13 ppbv / 17(14)% | 0.02 ppbv / 40(31)% | 0.069 ppbv | 0.0063 ppbv | 13 | 16 |

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show enhancements below 5 ppbv, while in the model 35 ppbv are reached at 60 km (not discernible from Fig. 5 due to the saturated scale which was chosen such that the MIPAS measurements can be analysed)."

**Figs 5 and 6** The model uses a pressure coordinate system at pressures below approx. 50 hPa, therefore the concerned figures, which use the MIPAS altitude axis as a vertical axis, do not show pure model levels. However, above 70 km the model vertical resolution is indeed very coarse and the top model layer contributes largely, resulting in the observed discontinuities. The reader is unlikely to obtain any useful information from this, so we have modified all Figures to only extend to 70 km.

**Section 4.1 N/NO production** "Does the total atomic nitrogen production change from the assumed 1.25Q wrt. altitude or is the branching between N($^2$D) and N($^4$S) altitude dependent?" The fitting procedure indicates that the total of N($^4$S)+NO production varies with altitude as does the branching between N($^4$S) and NO.

"The authors' approach is a bit worrying because it does not start from the known uncertainties of the involved processes but simply modifies the parameterisation for best results." Given the discussion on the work done on this subject (see above), for example an ion-chemistry model would be needed to be able to start such a study "from scratch". Note however that there are significant uncertainties for the involved reactions and reaction rates, and such a study would therefore be problematic as well. When new theoretical or experimental work will significantly reduce uncertainties, such an approach will be promising. For more details please see the discussion on the N/NO ratio above.

"Where does the proton energy go if not to production of atomic nitrogen by dissociation of $N_2$?" The protons lead to ionisations, dissociations, dissociative ionisations, and excitations. The ion and neutral odd-nitrogen chemistry is initiated by the action of energetic secondary electrons on $N_2$ and $O_2$., leading to various states of N, $N_2$, O, and $O_2$, which react further in a series of reactions. Finally, exothermic reactions transform the excess energy into thermal energy. For example, the reaction

$$\mathrm{e}^* + \mathrm{O}_2 \rightarrow \mathrm{O} + \mathrm{O}^+ + 2\mathrm{e} \tag{R7}$$

can be followed by

$$\mathrm{O} + \mathrm{O} + \mathrm{M} \rightarrow \mathrm{O}_2 + \mathrm{M} \tag{R8}$$

with a heat of reaction of -119.4 kcal/mole (Rusch et al., 1981; Brasseur and Solomon, 2005). Therefore, we can speculate that above 58 km where less energy is consumed in the production of N/NO, more energy results in chemical heating. However, chemical heating is not considered in EMAC and this process can therefore not be quantified with EMAC.

"Further, should the same N/NO production ratios be used when modeling electron precipitation, or are they just for protons?" While this is certainly an interesting question, this unfortunately cannot not be answered from the performed study. However, since secondary electrons are largely responsible for the occurring ion and neutral chemistry (see e.g. Rusch et al., 1981), it is possible that modeling electron precipitation in the same altitude region would require similar production ratios.

**Section 4.2 $NO_2$** "There is a better agreement between MIPAS and EMAC in Oct 30 and Nov 5 but in Nov 5 - Nov 10 the situation gets worse." See our reply to "Page 4510, lines 6-7" (above). With this in mind, the agreement between Fig. 4a and 10 is acceptable also in the latter period.

"I wonder if these models now become worse in $NO_2$ if the new parameterisation is used?" The new parameterisation was designed such that model/measurement differences in both $NO_2$ and $N_2O$ are minimized. While the changes in $NO_2$ mixing ratio from the original to the new parameterisation are generally less than 20% in the lower mesosphere (compare Fig. 4 and 10) and therefore of the same order of magnitude as the MIPAS $NO_2$ error, a slight improvement of $NO_2$ would be expected for other models also. Note that the HEPPA SPE model/data inter-comparison (Funke et al., in preparation) found $NO_2$ change discrepancies larger than 20% for most models.

"By the way, the N/NO ratio is reduced at all altitudes quite drastically (Fig. 9). One would expect that this would lead to increase of $NO_x$ because there is less N to react with NO ($NO_x$ loss). However, at least $NO_2$ is decreased." $NO_2$ is decreased only above approx. 55 km where the sum of N and NO per ion pair is reduced to less than 0.4, yielding less $NO_2$ and out-weighting the fact that less N is available to destroy NO.

**Section 4.2 $N_2O$** We modified the manuscript as follows: "In the observations, $N_2O$ enhancements reach 4.5 ppbv, which is overestimated by the model at approximately 6 ppbv. Note that at 50 km on 31 October, when the $N_2O$ mixing ratio maximises, the error is dominated by the systematic error of 0.25 ppbv. Assuming that the sampling error is smaller, there remains a bias between model and measurements."

**Page 4515, ozone** "However, when comparison the SPE/NO-SPE runs, there is long-term decrease above 60 km after the SPE." The decrease amounts to 0.5-1 ppmv of ozone. This is a result from elevated $NO_x$ concentrations in the mesosphere. This cannot be identified from Fig. 10 because in the model $NO_x$ mixing ratios drop from approximately 3 ppbv at the stratopause to 0.1 ppbv at 0.01 hPa. After the SPE the model mesospheric $NO_x$ mixing ratios are elevated at least until the end of November. E.g. at 20 November the $NO_x$ mixing ratio is still 3 ppbv at 0.02 hPa. We have attached a figure showing the percentage change of $NO_x$ mixing ratio for 70–90° N relative to 26 October. More than a 2000% increase at

70 km is evident until the end of November. This will be mentioned in the revised manuscript.

**Page 4516, lines 58-29 and Page 4517, lines 1-7** We agree that the original manuscript was not precise enough in the distinction of the short (during/days after the SPE) and medium-term (weeks after the SPE) effects and we have revised the concerned paragraph as follows: "Instead, the lack of cluster ion chemistry in EMAC is probably causing this disagreement. Stiller et al. (2005) found that after the conversion of $NO_x$ to $N_2O_5$ the latter reacts with cluster ions to form $HNO_3$. Since this reaction is not considered in EMAC, the $N_2O_5$ enhancements are much stronger than observed." "Indeed, EMAC simulations predict only an $HNO_3$ mixing ratio increase of 0.6 ppbv (see Fig. 7 in the supplement) in late November, compared to enhancements of 1–5 ppbv reported also by Lopez-Puertas et al. (2005) using MIPAS observations. Note that EMAC also does not reproduce the short-term increase of $HNO_3$ during and in the days after the SPE, similar to other models (see e.g. Jackman et al., 2008). As discussed by Verronen et al. (2008), the observed short-term increase is probably related to ion-ion recombination reactions missing in EMAC."

## References

Baumgaertner, A. J. G., Jöckel, P., and Brühl, C.: Energetic particle precipitation in ECHAM5/MESSy1 – Part 1: Downward transport of upper atmospheric $NO_x$ produced by low energy electrons, Atmos. Chem. Phys., 9, 2729–2740, 2009.

Brasseur, G. P. and Solomon, S.: Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere, Springer, third edn., 2005.

Crutzen, P. J., Isaksen, I. S. A., and Reid, G. C.: Solar proton events - Stratospheric sources of nitric oxide, Science, 189, 457–459, doi:10.1126/science.189.4201.457, 1975.

Dalgarno, A.: Atmospheric reactions with energetic particles, Space Research, 7, 849, 1967.

Fabian, P., Pyle, J. A., and Wells, R. J.: The August 1972 solar proton event and the atmospheric ozone layer, Nature, 277, 458–460, doi:10.1038/277458a0, 1979.

Funke, B., García-Comas, M., López-Puertas, M., Glatthor, N., Stiller, G. P., von Clarmann, T., Semeniuk, K., and McConnell, J. C.: Enhancement of $N_2O$ during the October/November 2003 solar proton events, Atmos. Chem. Phys., 8, 3805–3815, 2008.

Jackman, C. H. and McPeters, R. D.: Solar Variability and its Effects on Climate, vol. 141 of *Geophysical Monograph*, chap. The Effect of Solar Proton Events on Ozone and Other Constituents, pp. 305–319, American Geophysical Union, 2004.

Jackman, C. H., Douglass, A. R., Rood, R. B., McPeters, R. D., and Meade, P. E.: Effect of solar proton events on the middle atmosphere during the past two solar cycles as computed using a two-dimensional model, J. Geophys. Res., 95, 7417–7428, doi:10.1029/JD095iD06p07417, 1990.

Jackman, C. H., DeLand, M. T., Labow, G. J., Fleming, E. L., Weisenstein, D. K., Ko, M. K. W., Sinnhuber, M., and Russell, J. M.: Neutral atmospheric influences of the solar proton events in October-November 2003, J. Geophys. Res., 110, A09S27, 10.1029/2004JA010 888, doi:10.1029/2004JA010888, 2005.

Jackman, C. H., Roble, R. G., and Fleming, E. L.: Mesospheric dynamical changes induced by the solar proton events in October-November 2003, Geophys. Res. Lett., 34, L04 812, doi:10.1029/2006GL028 328, 2007.

Jackman, C. H., Marsh, D. R., Vitt, F. M., Garcia, R. R., Fleming, E. L., Labow, G. J., Randall, C. E., López-Puertas, M., Funke, B., von Clarmann, T., and Stiller, G. P.: Short- and medium-term atmospheric constituent effects of very large solar proton events, Atmos. Chem. Phys., 8, 765–785, 2008.

Jöckel, P., Sander, R., Kerkweg, A., Tost, H., and Lelieveld, J.: Technical Note: The Modular Earth Submodel System (MESSy) - a new approach towards Earth System Modeling, Atmos. Chem. Phys., 5, 433–444, 2005.

López-Puertas, M., Funke, B., Gil-López, S., von Clarmann, T., Stiller, G. P., Höpfner, M., Kellmann, S., Mengistu Tsidu, G., Fischer, H., and Jackman, C. H.: $HNO_3$, $N_2O_5$, and $ClONO_2$ enhancements after the October-November 2003 solar proton events, J. Geophys. Res., 110, A09S44, doi:10.1029/2005JA011051, 2005.

Porter, H. S., Jackman, C. H., and Green, A. E. S.: Efficiencies for production of atomic nitrogen and oxygen by relativistic proton impact in air, Journal of Chemical Physics, 65, 154–167, doi:10.1063/1.432812, 1976.

Rapp, D. and Englander-Golden, P.: Total Cross Sections for Ionization and Attachment in Gases by Electron Impact. I. Positive Ionization, J. Chem. Phys., 43, 1464–1479, doi:10.1063/1.1696957, 1965.

Rapp, D., Englander-Golden, P., and Briglia, D. D.: Cross Sections for Dissociative Ionization of Molecules by Electron Impact, J. Chem. Phys., 42, 4081–4085, doi: 10.1063/1.1695897, 1965.

Reid, G. C., Solomon, S., and Garcia, R. R.: Response of the middle atmosphere to the solar proton events of August-December, 1989, Geophys. Res. Lett., 18, 1019–1022, doi:10.1029/91GL01049, 1991.

Rusch, D. W., Gérard, J.-C., Solomon, S., Crutzen, P. J., and Reid, G. C.: The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere-I. Odd nitrogen, Planet. Space Sci., 29, 767–774, doi:10.1016/0032-0633(81)90048-9, 1981.

Stiller, G. P., Mengistu Tsidu, G., von Clarmann, T., Glatthor, N., Höpfner, M., Kellmann, S., Linden, A., Ruhnke, R., Fischer, H., López-Puertas, M., Funke, B., and Gil-López, S.: An enhanced $HNO_3$ second maximum in the Antarctic midwinter upper stratosphere 2003, J. Geophys. Res., 110, D20 303, doi:10.1029/2005JD006011, 2005.

Verronen, P. T., Funke, B., López-Puertas, M., Stiller, G. P., von Clarmann, T., Glatthor, N., Enell, C.-F., Turunen, E., and Tamminen, J.: About the increase of $HNO_3$ in the stratopause region during the Halloween 2003 solar proton event, Geophys. Res. Lett., 35, L20 809, doi:10.1029/2008GL035312, 2008.

Vitt, F. M. and Jackman, C. H.: A comparison of sources of odd nitrogen production from 1974 through 1993 in the Earth's middle atmosphere as calculated using a two-dimensional model, J. Geophys. Res., 101, 6729–6740, doi:10.1029/95JD03386, 1996.

Warneck, P.: Cosmic Radiation as a Source of Odd Nitrogen in the Stratosphere, J. Geophys. Res., 77, 6589–6591, doi:10.1029/JC077i033p06589, 1972.

Winters, H. F.: Ionic Adsorption and Dissociation Cross Section for Nitrogen, J. Chem. Phys., 44, 1472–1476, doi:10.1063/1.1726879, 1966.

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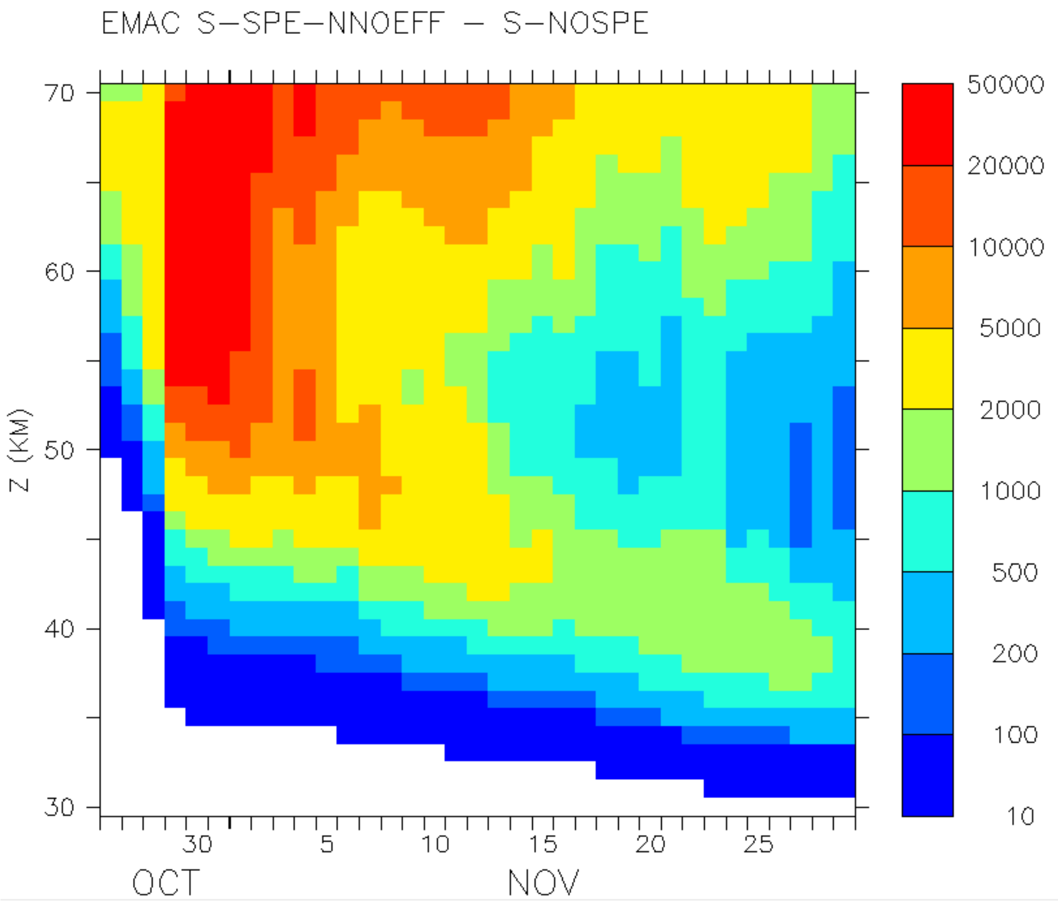

**Fig. 1.** NOx change at 70N-90N in percent with respect to 26 October.

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