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Interactive Comment

Interactive comment on "Lifetime and production rate of NO_x in the upper stratosphere and lower mesosphere in the polar spring/summer after the solar proton event in October–November 2003" *by* F. Friederich et al.

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First, the authors would like to thank the referee for his careful review of our manuscript and his helpful and constructive comments. In the following I reply to each of the comments on behalf of all co-authors. The reviewer comments are given in black while our reply is provided in blue.

Abstract, line 2, altitude-dependent instead of altitude dependent

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everywhere corrected

Abstract, line 9 and in other places, -63S refers to Southern Hemisphere with both - and S. Use either - or S (better use the latter).

everywhere corrected

Page 17705, line 2. Ionization takes place also below 40 km, especially during solar proton events (SPE). However, even during large SPEs ionization rates do not increase much below 30 km, because at those altitudes there is always ionization caused by galactic cosmic rays which dominates.

We don't want to mention that E $>$ 500MeV particles can even reach the tropopause, because it's not relevant for this study. So we write: "Propagating along the interplanetary field lines the energetic particles (protons, electrons and a few more massive ions) may reach the Earth and precipitate - guided by the terrestrial magnetic field - in the polar cap regions where they cause ionization in the mesosphere and stratosphere." (Introduction, line 32-36)

Page 17705, line 5.: Why focus on altitudes 42-62 km only? I think the answer is that this is the altitude region which is affected by protons AND is covered by MIPAS observations. The "Focussing" part should be moved, as a last paragraph, with added explanations.

This part was moved to the beginning of the second last paragraph with added explanations: "We focus on altitudes between 42 km and 64 km, because this region is both affected by the SPE and covered by MIPAS observations." (Introduction, line 94-96)

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Page 17705, line 10, whole paragraph. Are all these reaction details really needed here? Are they used later in the paper?

in our opinion yes, after little changes Reacts. (R2)-(R8) are also mentioned later in the paper.

- (R1)–(R4): most important NO production
- (R5)+(R6): NO $\longleftrightarrow$ NO_2 diurnal cycle. Now mentioned additionally in Introduction, line 103: "While the lifetime of NO and NO_2 is shorter than a day due to Reacts. (R5) and (R6), the lifetime of NO_x is typically a few days at altitudes from 42 km to 64 km at sunlit conditions (Brasseur and Solomon 2005)."
- (R7)+(R8): most important NO loss reactions

In addition to Porter (1976), there is a paper by Rusch et al. (1981) which concludes a similar number N-atoms per ion pair. Other studies have given a range of possible numbers, see e.g. discussion in Baumgaertner et al. (2010). It would be good to mention these studies, although 1.25 is the generally accepted number, as it would put the results of this paper in wider context.

following was added: "Rusch et al. (1981) found a N-production rate between 1.3 and 1.6. with an 80 % branching ratio for production of $N(^2D)$. Baumgaertner et al. (2010) found altitude-dependent N-production rates between 0.0 and 0.3 and NO-production rates between 0.2 and 1.2." (Introduction, line 50-54)

Page 17706, paragraph starting from line 5: The chemical lifetime of NOx is a few days in sunlit conditions, at night or during polar winter the lifetime is more like months.

following was added: "While the lifetime of NO and NO_2 is shorter than a day due to Reacts. (R5) and (R6), the lifetime of NO_x is typically a few days at altitudes from

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42 km to 64 km at sunlit conditions (Brasseur and Solomon 2005).” (Introduction, line 96-99)

Some justification should be given: why was this study made and what are the objectives?

“Model-measurement comparisons have revealed several discrepancies, but facing the complexity of the models it is not always easy to isolate the responsible process for the model-measurement difference. To this end, we use NO_x-production rates and lifetimes as model diagnostics and provide these data based on MIPAS measurements. Because this SPE is the strongest MIPAS has measured, it can be used as an experimental examination of the NO_x-production rate and the altitude-dependent lifetime of NO_x.” (added to Introduction, line 85-93)

Section 2.1. Some more information on the MIPAS data could be given. As I understand it, NO is not one of the standard MIPAS products and is not provided by ESA. Therefore, it would be interesting for the reader to have more information on the NO product. I suppose NO data are available for limited time periods only?

- the retrieval is described in Funke et al. (2005a), improvements in Funke et al. (2011) (added to Sect. 2.1, line 138 + 153)
- “NO and NO_2 are products of the Institute of Meteorology and Climate research (IMK) and of the Instituto de Astrofisica de Andalucia (IAA). Both trace gases are available for the full mission period (with exception of April - December 2004).” (added to Sect. 2.1, line 147-151)

How accurate are the NO data in the stratosphere? There is a lot of NO in the 110 km region which would be in the line-of-sight of every measurement?

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"Because there is a lot NO in the 110 km region which is in the line-of-sight of every limb scan, the data are corrected for by joint-fitting the thermospheric column. The accuracy is better than 15% (Funke et al., 2005a)." (added to Sect. 2.1, line 158-162)

I do not understand the last paragraph. I assume that the authors are taking zonal averages at selected latitude bands.

Due to Referee Comment # 1, we do not take latitude bands any more, but the whole polar cap. Following was added: "In the analysis, we take zonal averages of vmr and the number density n ($\overline{\text{vmr}}$ and $\overline{n}$) of the polar cap between 50°S and 90°S." (Sect. 2.1, line 158-162).

The last sentence needs an explanation: why is the AVD diagonal element an important criterion?

"When mean(AVD) is smaller than 0.03, mean(vmr) depends strongly on its a priori value of the retrieval." (added to Sect. 2.1, line 168-169)

For clarity, please use AVK and AVD instead of avk and avd.

done

About calculating the averages: the authors should give some more information. For example, number of data points, standard deviation/error (the error is shown in the figures, but it would be good to also discuss these briefly here).

"The six-hour zonal means of the vmr we use in Sect. 3.1 are calculated by maximum 61 geolocations. Especially at the days during the SPE the number of geolocations we use is mostly reduced to about 35-40 geolocations. The standard error of the mean is dependent on the number of geolocations and thus bigger during the SPE but

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mostly lower than 10 %. The 24-hour zonal means of the NO_x-number density we use in Sect. 3.2 are calculated by maximum 211 geolocations and mostly more than 150 geolocations. The standard error of the mean is always lower than 1 %, besides at the days during the SPE (lower than 5 %)." (Sect. 2.1, line 169-180)

Section 2.2, line 5. remove the IPP here. The ionization rate units are cm-3 s-1.

corrected (line 198+199)

Fig 1. The authors could add another panel showing the observations and the fit for another altitude, say 45 km. This would help to demonstrate the differences between altitudes.

- new Fig. 1: 45km + 62km
- new explanations in caption: "MIPAS vmr measurements of NO_x (red) at October-November 2003 and a fit of an exponential function (blue) between 50°S and 90°S and at 62 km (top) and 45 km (bottom) altitude. The error bars show the error of the mean of the zonal averages."
- new in Sect. 3.1 (line 218-220): "Fig. 1 shows 6 h-averaged MIPAS measurements with the standard error of the mean (error bars) at altitudes of 45 km and 62 km."

Page 17709, line 5. X**2 should be explained much better, now it is not clear what it exactly is and how it should be interpreted. I assume that X**2 is the residual, but the authors do not say this!

- yes, it's the reduced residual.

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- new in Sect. 3.1 (line 223-224): “The corresponding reduced residuals (χ^2) between measurement and fit are shown on the right.”
- new in Sect. 3.2 (line 356-358): “The altitude-dependent reduced residuals (χ^2) of the fits is shown in the right-hand figure.”

Page 17709, from line 25 on. The result here is that in general the dynamical lifetime is shorter than the photochemical one, i.e. transport and mixing explain most of the observed NOx behavior. Is this a typical situation? The authors could give some more details on the dynamical conditions. Especially, they should explain the longer dynamical lifetimes at 73S, 50-55 km. Is this related to the orientation of the polar vortex (I know that it might be already gone by October).

“At 54 km altitude, there is a local maximum of the lifetimes. During the SPE, the polar vortex in the Southern Hemisphere was already gone, so it cannot be responsible. Nevertheless in these altitudes dynamical transport is apparently less effective. It also plays a role, that React. (R2) is more effective near the stratopause than at other altitudes due to the strong temperature-dependency. So N(^{4}S), which is produced by photolysis, prefers React. (R2) rather than React. (R8). Therefore the photochemical lifetime can become longer.” (Sect. 3.1, line 265-274)

Page 17710, line 11-19. This text could be already in the introduction, as a part of a paragraph briefly describing this study.

done (added to Introduction, from line 106 on): “Downward transport of upper atmospheric air...”

IPP (ion pair production) is defined many times, only do it once when it is first used.

done

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Section 3.2 needs to be rewritten in order to make it more readable and understandable. Clearly not enough details are given.

It has been rewritten, see the next points and Referee Comment # 1

For example, I do not understand how Eq.4 can be used for the whole time series of 250 days (as shown in Fig. 3). Surely the NOx lifetimes (photochemical, dynamical, and total) will change considerably within the 8-month time period. The authors then fit a line to all the data points (in Fig. 3r), which means that most of the points have little IPP or corresponding NOx production. Would it not be more appropriate to use a smaller set of points from the SPE period? These issues should be carefully discussed and the approach taken should be justified.

- To determine the background reliably it is necessary to look at a longer period. Following was added: "To do this reliably the period from 1 October 2003 until 31 March 2004 is fitted." (Sect. 3.2, second paragraph, line 302-303)
- To determine the NO_x production, only a period of 60 days is of strong relevance (Fig. 3 right). This point was already made but not well described. This is now rectified: "Only days of strong relevance are plotted (25 October - 31 December 2003)." (Sect. 3.2, line 334-336)
- yes, the NO_x lifetimes can change and is discussed:
  - "There is another noticeable discrepancy regarding the NO_x-enhancement after 20 November (indicated by orange symbols). Either the effective production rate of NO_x is higher under the certain conditions of the 20 November or the lifetime of NO_x became significantly longer (altitude-dependent up to a factor 1.5)." (line 346-352)
  - "Calculations with a shorter lifetime (-33 %) lead to a higher effective production rate (about 30 %)." (line 388-389)

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I(IPP,tau,t0) given in Eq. 5 should be explained better, how to interpret it and how it will vary with time.

- Eq. 5 changed to Eq. 4
- "A theoretical determination of the NO_x-number density enhancement requires the correct accumulation of the previous IPP, because the NO_x-lifetime τ is several days long (Sect. 3.1). The accumulated ion pair production $I(\mathrm{IPP}, \tau, t_0)$ takes into account NO_x-loss processes by weighting the previous IPP with an exponential loss function depending on the quotient of the time difference $t_0 - t$ and the NO_x-lifetime τ:

$$I(\mathrm{IPP}, \tau, t_0) = \int_{-\infty}^{t_0} \mathrm{IPP}(t) \cdot e^{-\frac{t_0 - t}{\tau}} \mathrm{d}t. \tag{4}$$

" (Sect. 3.2, line 311-319)

Why it's useful to plot the difference of NOx with respect to I(IPP,tau,t0)?

"In order to examine whether the measured enhancement of the NO_x-number density $\Delta n_{\mathrm{MIPAS}}$ can be determined by [the theoretical quantity] $I(\mathrm{IPP}, \tau, t_0)$, Eq. (5) is modified to:

$$\Delta n_{\mathrm{MIPAS}}(\mathrm{IPP}, \tau, t_0) = x \cdot \frac{\mathrm{NO_x}}{\mathrm{ionpair}} \cdot I(\mathrm{IPP}, \tau, t_0). \tag{6}$$

" (Sect. 3.2, line 326-329); the plot shows the results of this equation.

Page 17711, from line 20 on, related to the previous comment. If I(IPP,tau,t0) increases but NOx does not, it could also indicate that the NOx lifetime is shorter than estimated. On November 20, if the NOx lifetime was longer than estimated a month before, it would lead to a behavior similar to that seen in Fig. 3. These possibilities should be discussed.

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- days before the SPE (yellow crosses): If the reason was a shorter lifetime, the lifetime would be so short, that MIPAS can't see an increase of NO_x (lifetime $<$ few hours). This is very unlikely.
- November 20: with a 2 times longer lifetime these differences could be explained. Following was added: "Either the effective production rate of NO_x is higher under the certain conditions of the 20 November or the lifetime of NO_x became significantly longer (altitude-depentend up to a factor 1.5)." (Sect. 3.2 line 348-352)

Fig 3. Standard error of the mean is not visible. If this is because they are so small, then remove them from the plot and give a typical number in the caption or text.

Removed from the figure. Following was added to the caption: "The standard error of the mean of the number densities is always lower than 1 %, besides the days during the SPE (lower than 5 %)."

Page 17712, line 10. "Most of the X**2 values are significantly larger than one and so they argue for a non-linear NOx-production." This statement is mystifying, it does not tell anything to the reader. Larger X**2 values mean a poorer fit, right?

Reformulated: "Most of the χ^2 values are significantly larger than one. Higher χ^2 values argue for a poorer fit and thus for a non-linear NO_x-production. This means that the effective NO_x-production is dependent on the existing NO_x-number density, which was already shown in Funke et al. (2011)." (Sect. 3.2, line 358-362)

Line 12, "This is obvious,: : :". It is obvious, because 1.25 only considers production, while the authors consider also chemical and dynamical loss (thus "effective" NOx production rate).

"The effective NO_x-production rate is significantly lower than the N-production rate 1.25 at all altitudes. This is obvious, because the 1.25 only considers the production of

N(^{4}S) and N(^{2}D) while the effective NO_x-production rate in the study considers both N-production and the chemical loss by React. (R8). Following relation applies to the production p:

$$1.25 = p(\mathrm{N}(^4\mathrm{S}) + \mathrm{N}(^2\mathrm{D})) > p(\mathrm{NO} + \mathrm{NO_2}). \qquad (7)$$

Dynamical or photochemical NO_x-loss processes are compensated through $I(\mathrm{IPP}, \tau, t_0)$ [Eqs. (4)+(6)] and do not influence the difference between the NO_x-production rate and the effective NO_x-production rate." (Sect. 3.2, line 363-373)

Fig. 4. The authors have shown (Fig. 2) that the NOx lifetime decreases with increasing altitude. That should mean that their effective NOx production rate should also decrease with altitude. However, in Fig. 4 the authors are showing the opposite: the effective NOx production rate is lower at lower altitudes. It is quite difficult to understand what is going on here.

The lifetime-dependency is contained in I(IPP,tau,t0). Therefore the production rate is not be dependent on the lifetime (Eq. 6). The effective production rate is mainly dependent on the altitude-dependency of Reaction 8. I think it should be comprehensible after the reformulation due to the comment, five points above: "Why it's useful to plot the difference of NO_x with respect to I(IPP,tau,t0)?"

Another figure like Fig. 3, but at 45 km, should be shown.

- new Fig. 3: 45 km+56 km.
- following was added:
  - "Both $n(\mathrm{IPP}, t_0)$ and $n(\mathrm{IPP} = 0, t_0)$ are shown in Fig. 3 (left) as crosses and as a green graph, respectively, for altitudes of 45 km and 56 km." (Sect. 3.2 line 304-306)

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- “In Fig. 3 (right) $\Delta n_{\text{MIPAS}}(t_0)$ is plotted over $I(\text{IPP}, \tau, t_0)$ at altitudes of 45 km and 56 km. Only days of strong relevance are plotted (25 October - 31 December 2003).” (line 333-336)
- The caption of Fig. 3 was modified accordingly.

The authors do have a possible explanation, too high ionization rates, but this is only mentioned in the abstract and conclusions, while a real discussion on this matter is missing. It seems to me that the ionization rates should be a factor of 5 (3) too high to explain 0.2 at 45 km (0.3 at 50 km).

“The high discrepancies between theoretical and empirically determined values can be composed of different error sources:

- Systematic NO_x retrieval errors up to 15 % (Sect. 2.1).
- Production rates of high energetic electrons are overestimated. We did the same calculation without electron ionization (blue squares, Fig. 4, left). Between 58 km and 62 km altitude, electron ionization is needed. Between 52 km and 56 km this effect could explain the discrepancies and between 44 km and 50 km altitude this effect could only explain between 5% and 25% of the discrepancies.
- Calculations with a shorter lifetime (-33 %) lead to a higher effective production rate (about 30 %).

Known error sources can explain the discrepancies between 52 km and 62 km. To explain the discrepancies for altitudes between 44 km and 50 km, a change in the proton ionization rates, in the N-production rate, or in the N(^{2}D)-N(^{4}S)-branching ratio is needed.” (Sect. 3.2, line 376-394)

Does this result agree with the earlier studies?

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It agrees only qualitatively with studies of Funke et al. (2011). Following was added: “A test without electron ionization rates (blue symbols) showed that the discrepancy cannot be explained only by this effect, which is also only qualitative in accordance to the WACCMp model run of their study.” (Sect. 4.2, line 456-459)

Section 4 has very little meaning. The authors try to compare their results, NOx lifetime (NOxLT) and "effective" production rate due to particle precipitation (EPR), with previous studies. However, they do not compare anything with Jackman (2005) results, they simply state Jackman’s results. A comparison would not be possible anyway, because Jackman’s study did not consider NOxLT or EPR.

We agree with this reviewer and decided to remove the comparison to the Jackman et al. (2005) results.

A comparison with Baumgaertner (2010) is possible, because they also presented EPR (but only considering effective production of N and NO, and not, e.g., dynamical losses). However, the authors mostly describe what Baumgaertner did and then take care of the comparison with one sentence. They do not discuss any of the possible reasons behind the differences.

Baumbaertner et al. calculated N- and NO-production rates, not effective production rates. Now, we have used them to calculate effective NOx-production rates. The reasons for the differences are mentioned now:

“We used these altitude dependent N- and NO-production rates to calculate effective NO_x-production rates with the box model, described in Sect. 4.1. This is shown as a violet dashed line in Fig. 4 (left). Differences to the black line are only caused by the differences due to the altitude-independent NO_x-production rate of Porter et al. (1976). These differences do not show a clear approximation to the effective NO_x-production rates calculated in Sect. 3.2. Their effective NO_x-production rates are two to five times

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higher at altitudes from 44 km to 54 km and significantly lower at 60 km and 62 km. At 56 km and 58 km altitude error bars overlap. These differences have most likely different reasons. The authors fit the N_2O abundance, while in our study, the NO_x abundance is fitted. This can lead to discrepancies. Then, they look at the Northern Hemisphere, which has other conditions regarding temperature, dynamics, and gas abundances than the Southern Hemisphere. Finally, they do not account for dynamics, but this should be of no consequence, because due to Eq. (4) loss processes (dynamical and photochemical) are compensated in our calculations." (Sect. 4.2, line 476-495)

Funke (2011) also presented EPR (but did not consider dynamical loss), which is shown to decrease with increasing altitude (above 45 km). In the current paper, the authors show an opposite altitude behavior (see the previous comment), but do not bother to properly discuss the possible reasons. This section needs to be completely rewritten.

- As mentioned above, in our calculations of the effective production rates, dynamical loss processes are compensated: "Dynamical or photochemical NO_x-loss processes are compensated through $I(\text{IPP}, \tau, t_0)$ [Eqs. (4)+(6)] and do not influence the difference between the NO_x-production rate and the effective NO_x-production rate." (Sect. 3.2, line 370-373)
- We see no different behaviour than Funke et al. (2011). (See also the answer to the previous comment: "Fig. 4. The authors have shown (Fig. 2) that the NO_x lifetime decreases with increasing altitude.")
- Due to this reasons, we think, the statements of the discussion paper are right.
- following was added:
  - "Transport is not considered, but this should be of no consequence as mentioned above, because in our determination of the effective production rates

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in Sect. 3.2, loss processes due to transport are compensated." (line 429-432)

- The discrepancies between measured and modelled NO_x-production rates at altitudes between 44 km to 52 km are only in qualitative accordance to the results of the HEPPA intercomparison. The discrepancies in that intercomparison are much lower. A test without electron ionization rates (blue symbols) showed that the discrepancy cannot be explained only by this effect, which is also only qualitative in accordance to the WACCMp model run of their study. (line 455-459)

The authors give a brief and vague conclusion for their study. What is the reason this study was made?

"We have derived effective NO_x-production rates and NO_x lifetimes directly from the measurement, in order to provide model diagnostics." (Conclusions, line 497-499)

What are the questions to be answered?

- Dependency of NO_x lifetime? - NO_x lifetime depends on dynamics very strongly.
- Is there a way to determine the production rate out of the measurements? - yes, but only the effective production rate
- Are the results in qualitative agreement with former studies? - Calculation of the production rate above 56 km is in accordance to theoretical values. Below 54 km, error sources cannot explain the differences to theoretical values. This is in qualitative agreement with former studies.

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Do the results have any meaning, e.g., for atmospheric modelling? Where is the improvement? Should we change the current parameterization of NOx production? The results are not properly discussed in context.

- “The effective NO_x-production rate and the NO_x lifetime we determined can be used as model diagnostics for model-measurement comparison.” (line 511-513)
- Before changing the parameterization more studies are needed.

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