**Atmospheric
Chemistry
and Physics
Discussions**

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.

Section 3.1: The authors mentioned that "vertical advection is small in polar summer",

but is this really the case? First of all October-November is not the summer yet, polar night jet can still exist. Even during the summer the polar mesopause is very cold due to enhanced upwelling caused by gravity waves. I guess, this suggestion should be better supported and explained.

Yes, upwelling can exist in polar summer. But we want to point out, why we exclude the Northern Hemisphere: the impact of dynamics on NO_x vmr is much stronger when polar jet exists compared to other times of the year (e.g. Funke 2005b). We reformulated that part (compare also the reply to Reviewer #2): "Downward transport of upper atmospheric air has a huge impact on NO_x in the winter hemisphere (Siskind and Russell, 1996; Funke et al., 2005b; Randall et al., 2007). During polar winter, air intrudes in the mesosphere from above and elevates the volume mixing ratio (vmr) of NO_x about several orders of magnitude through the indirect energetic electron precipitation (EEP) effect. Smaller enhancements due to the EEP impact cannot be easily distinguished from the descending NO_x-rich air masses. Thus, we analyze only data from the Southern Hemisphere where vertical motion is upward during the period under investigation and descended NO_x-rich air masses from the previous winter have already disappeared." (added to introduction, line 106-118)

The authors also excluded "..any important NOx production during..." This assumption should be also explained, because the reaction N2O+O(1D)= NO+NO can be important during the late spring and summer.

- Due to the large NO_x-enhancement caused by the SPE, this chemical reaction plays a smaller role for the determination of the lifetime.

- This chemical reaction is a continuous source, unlike the SPE.

- "any important change of the usual NO_x production" was added: "In our idealized assumption, the source of NO_x is inside the polar caps due to the SPE and there

is no NO$_x$ enhancement outside the polar caps nor any important change of the usual NO$_x$ production without SPE during the three days after the SPE." (added to Sect. 3.1, line 238-242)

The calculated lifetime is separated into transport and photolytic. However, the photolytic life time was not properly introduced and it is not clear what processes are behind this term.

- Processes behind the terms: photolytic: NO+h$\nu \rightarrow$ N+O (R7), and photochemical: photolytic and N(^{4}S)+NO $\rightarrow$ N$_2$+O (R8).

- Photolytical loss is 1 NO per photon.

- Photochemical loss can vary between 0 and 2 NO per photon.

- Following was added: "In our study we distinguish between the photolytical loss due to React. (R7) and the photochemical loss due to Reacts. (R7) and (R8). Depending on whether React. (R2) or React. (R8) dominates, photochemical loss can vary between zero and two NO per photon." (added to Introduction, line 76-80)

It is not described how this quantity is calculated using SLIMCAT model and how accurate this calculations are.

- "SLIMCAT calculates photolysis rates $J = \frac{1}{\tau_{\text{phot}}}$ by interpolating precomputed J of a four-dimensional (pressure, temperature, O$_3$ column, and solar zenith angle) look-up table. The absorption cross section of NO is taken from Minschwaner and Siskind (1993). They give an uncertainty of '30-40 % in the stratospheric photolysis rate'." (Sect. 3.1, line 249-253)

- The Minschwaner and Siskind (1993) paper was also added in References.

The role of reaction R8 is not discussed. This reaction is not related to transport and photolytic (because N(^{4}S) and NO are the products of ionization by particles), so the authors should explain why R8 is neglected.

the role is now discussed by following additional explanations:

- Abstract: "photolysis" is replaced by "photochemistry"; "dynamical lifetimes" is replaced by "estimates of dynamical lifetimes": "The lifetimes are controlled by transport, mixing and photochemistry. We infer estimates of dynamical lifetimes by comparison of the observed decay to photolytical lifetimes calculated with the SLIMCAT Model." (line 6-9)

- Introduction: "In our study, we distinguish between the photolytical loss due to React. (R7) and the photochemical loss due to Reacts. (R7) and (R8)." (line 81-83)

- Sect. 3.1: "Lifetimes calculated by the photolysis rates are a lower limit for the lifetimes due to photochemistry. Thus the calculated dynamic lifetimes τ_{dyn} are an upper limit." (line 258-261)

- (R8) is discussed, whenever we describe the difference between the production rate and the effective production rate. For example: "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)." (Sect. 3.2, line 363-368)

The authors conclude that the transport play a major role in the decay of SPE generated NOx almost everywhere except 73 deg. south between 50 and 55 km. It is interesting

feature, but the authors do not even try to explain what could be the reason for the absence of transport processes there.

"During the SPE, the polar vortex 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 $N(^4S)$, which is produced by photolysis, prefers React. (R2) rather than React. (R8). Therefore the photochemical lifetime can become longer." (added to Sect. 3.1, line 266-274)

I think it would be interesting to analyze the decay of NOx integrated over entire southern high latitudes. This analysis would exclude the local transport and could show how good the calculation of photolytic (whatever it means) NOx removal is:

- photolytic NO_x removal means that it is controlled by $NO+h\nu \rightarrow N+O$ (R7).

- Due to this comment we changed our analysis from different zonal means to the whole polar cap (50S–90S). The data were calculated again and the figures are new. Figure captions and descriptions in the text were adapted.

Section 3.2: This section is a little bit difficult to read because the explanations are too short.

compare also the reply to Reviewer #2

For example the authors say "n(IPP=0, t0) can be determined by means of a polynomial function, fitted to the MIPAS data of the Austral summer 2003/2004", however the analyzed period starts in October and the line in the Figure 3 starts 150 days before 1 January. Does it mean that the summer data were extrapolated to winter time?

We leave the word "summer" out and write the correct date instead of that: "To do this reliably the period from 1 October 2003 until 31 March 2004 is fitted." (added to Sect. 3.2, line 302-303)

The text says "the color code is time dependent", but there is no explanations at all how to read these colors.

"The color code of the crosses is time dependent: at days before the SPE the crosses are green and yellow. During the SPE they are orange and merge to red until the end of December. Days in 2004 are dark (black to blue)." (added to Sect. 3.2, line 306-310, and also in the caption)

The discussion of two branches is hard to follow, I have problem trying to identify which branch has observable gradient.

In response to Reviewer #2 this part had to be reformulated. We don't write about branches in this figure any more.

The discussion about another noticeable discrepancy after 20 November is also difficult to understand, because it is too short.

"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)." (added to Sect. 3.2, line 348-352)

The same can be said about the Figure 3 (right) and the explanation how this data were calculated.

Reformulated: "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:

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

The enhancement of the NO_x-number density $\Delta n_{\mathrm{theory}}$ due to $I(\mathrm{IPP}, \tau, t_0)$ at the time t_0 can thus be determined theoretically by assuming a production rate of 1.25 NO_x per ion pair:

$$\Delta n_{\mathrm{theory}}(\mathrm{IPP}, \tau, t_0) = 1.25 \cdot \frac{NO_x}{\mathrm{ion\ pair}} \cdot I(\mathrm{IPP}, \tau, t_0). \tag{5}$$

" (Sect. 3.2, line 311-324)

I do not really understand Equations 4 and 5. In particular, these equations are almost identical (except the coefficient before the integral), but why in the Eq.4 the values depends only on t0, while in eq.5 it is a function of IPP, tau and t0.

Eq. (4)+(5) both depending on τ and t_0 now and were rewritten (see above).

It confuses a bit when you try to understand Figure 3 (right). I would be very appreciated if this part is explained with more details.

New in the paper: "In order to examine whether the measured enhancement of the

NO_x-number density $\Delta n_{\mathsf{MIPAS}}$ can be determined by $I(\mathsf{IPP}, \tau, t_0)$, Eq. 5 is modified to:

$$\Delta n_{\mathsf{MIPAS}}(\mathsf{IPP}, \tau, t_0) = x \cdot \frac{\mathsf{NO_x}}{\mathsf{ion\ pair}} \cdot I(\mathsf{IPP}, \tau, t_0).$$
(6)

x is the altitude-dependent effective production rate of NO_x per ion pair replacing the theoretical value of 1.25, and is empirically determined in the following." (Sect. 3.2, line 326-332)

Section 4.1 is not instructive at all. It is not clear what the authors would like to convey. It can be easily moved to introductions.

In response to Reviewer # 2 this is left out.

In section 4.2 the authors try to compare (I guess) different things: the effective NOx production rate from Fig.4 calculated from the observed decay of NOx after SPE taking into account all processes in the atmosphere and the coefficient of N and NO production associated with the formation of ion pair. I am not sure that this comparison is well justified.
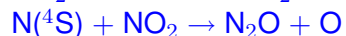
Baumgaertner et al. (2010) determined (initial) N- and NO- production rates. Using them we calculated effective NO_x-production rates and compared them with our results. Following was added/changed: "We used these altitude dependent N- and NO-production rates to calculate effective NO_x-production rates 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 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." (Sect. 4.2, line 476-487)

In the subsection 4.3 I suggest to introduce better the applied box model. Otherwise, the reader will have to read long Funke et al. (2011) paper where this box model is introduced (in my opinion even in this paper the box model was not properly described). In particular, how the transport is treated in the box model (the authors showed earlier that the transport processes play a major role in NOy decay).

This section changed to Sect. 4.1.

"The model considers temperature, Reacts. (R2), (R3), (R5)-(R8), and following reactions:

$NO_2 + O \rightarrow NO + O_2$
$N(^4S) + NO_2 \rightarrow N_2O + O$
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_2 + NO \rightarrow 2 \cdot NO_2$
$O + O_2 \rightarrow O_3$
$NO_2 + NO_3 \rightarrow N_2O_5$.

In addition the box model accounts for ionization rates. Transport is not considered, but this should be of no consequence as mentioned above, because in our determination of the effective production rates in Sect. 3.2, loss processes due to transport are compensated." (added to Sect. 4.1, line 420-427)

It is interesting to note that the results obtained by the authors substantially disagree

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with the Funke et al. (2011) results for day time conditions. Dashed black curve from Fig.13 of Funke et al. (2011) looks similar to green symbols in Figure 4 and differs from black line. The authors do not try to explain the possible reasons for such a difference.

This is caused by the different temperature profile in the Southern Hemisphere. It depends on temperature whether $N(^4S)$ reacts with O_2 (R2) or with NO (R8): "The shape of the black curve is explained by React. (R2) which is strongly temperature-dependent. It is less effective in colder and therefore higher altitudes in the mesosphere. Compared to the Northern Hemisphere (i.e. Funke et al. (2011)), the Southern Hemisphere is $60\,°K$ warmer at $40\,km$ ($3\,hPa$) altitude and $40\,°K$ warmer at $50\,km$ ($1\,hPa$). At $60\,km$ ($0.2\,hPa$), there is no big difference in temperature." (Sect. 4.1, line 440-448)

Conclusions: The conclusions are even shorter the abstract! The authors concluded that "The calculated NOx-production rates do not reproduce the theoretical value of 1.25 ...". This conclusion is obvious (as the authors mentioned in the earlier text) and I do not think it is hopefully not the main conclusion of the paper. The discussion about the comparison with Funke et al. (2011) is vague and not instructive. The discussion about possible overestimation of the IPP by AIMOS model is interesting, but again too short. What is missing here is some discussion/outlook of how the models can be better validated using presented MIPAS data analysis and how to find a way to confirm simple parametrization used in most of CCMs.

Also in response to Reviewer # 2, following points were added:

- We have derived NO_x lifetime and production rate directly from the measurement, in order to provide model diagnostics.

- NO_x lifetime depends on dynamics very strongly.

- The effective production rates are not comparable with the theoretical production rate because of React. (R8).

- Calculation of the effective production rate above 50 km is in accordance, below 50 km, error sources cannot explain the differences.

- The effective NO_x-production rate and the NO_x-lifetime we determined can be used as model diagnostics for model-measurement comparison.

- NO_x production rates may be overestimated below 50 km.

Minor comments and technical corrections:

1. Page 17709, line 7: it should be "there" instead of "they"?

No, "they" is right.

2. Page 17714, lines 1-4: Please reformulate. It reads like the electrons are measured at the altitudes around 50 km.

done