

## ***Interactive comment on “Mesospheric nitric oxide model from SCIAMACHY data” by Stefan Bender et al.***

We thank the reviewer for the careful review of the manuscript. We have marked our replies in blue and changes made in the paper in green .

### **Anonymous Referee #1**

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This paper uses mesospheric NO observations taken by the SCIAMACHY instrument between 2002 and 2012 to build a non-linear empirical model of NO number densities as function of time and geomagnetic latitude, driven by the AE index as proxy for energetic particle precipitation and the Ly- $\alpha$  index as proxy for the EUV and XEUV influences.

The presented empirical model is very useful for constraining or validating atmospheric models and complements other empirical models of NO that focus either on the lower thermosphere or on the stratosphere/lower mesosphere.

The paper is generally well written and the methodology is presented in a clear manner. However, the discussion of the obtained responses could be improved by consideration of the limitations of the empirical model. For instance, modeled responses are interpreted as NO production rates (e.g., the AE response) which is an oversimplification since important physical mechanisms are not represented by the model (e.g., transport). Similarly, many of the discussed hemispheric asymmetries are most likely related to the use of geomagnetic coordinates (see specific comments below). This should be addressed before publication in ACP.

We address the issues raised in our replies to the specific comments below.

Specific comments:

p2 l4: This is misleading: SSWs cause reduced mesospheric descent (or even an upwards motion), not enhanced descent. You are referring to the strong downwelling that often occurs in the recovery phase of the SSW, typically associated with the formation of an elevated stratopause.

We thank the reviewer for the pointer and changed the sentence accordingly:

“Additional dynamical processes also result in a strong downward transport of mesospheric air into the upper stratosphere, such as the strong downwelling that often occurs in the recovery phase of a Sudden Stratospheric Warming (SSW) (Orsolini et al., 2017; Pérot et al., 2014). This downwelling is typically associated with the formation of an elevated stratopause.”

p2 l9: MIPAS upper atmosphere observations were carried out in the 40 - 170 km range, see Bermejo-Pantaleón et al., 2011 (doi:10.1029/2011JA016752).

Indeed, Bermejo-Pantaleón et al., 2011 states an altitude range of 42–172 km for the MIPAS UA observations. We changed the numbers in the text and added (Bermejo-Pantaleón et al., 2011) to the citations.

p2 l19: I wouldn't say the most CCMs parametrize NO. Rather, some models (those that are not resolving the thermosphere) constrain NO at the models upper lid by observation-based parameterizations.

We agree with the reviewer and to clarify, we changed the sentence in question to read:

“...some models constrain the NO content at their top layer by observation-based parameterizations.”

We also added a reference to (Funke et al., 2016) after “...Envisat/MIPAS NO measurements” in the next sentence since this parameterization is suggested in (Matthes et al., 2017).

p3 l5: Is there any atmospheric model study that illustrates the effectiveness of NO<sub>x</sub> photo-excitation as NO loss process? I would expect that N<sub>2</sub>O formation via metastable N<sub>2</sub>(A) +O<sub>2</sub> as discussed in Funke et al. 2007 and Sheese et al., 2016 is likely a more relevant source for upper atmospheric N<sub>2</sub>O.

We agree with the reviewer that a thorough study has yet to be carried out. To explain the possible connection between N<sub>2</sub>O and our study, we have changed and extended the discussion after reaction (R5) to:

“N<sub>2</sub>O has been retrieved in the mesosphere and thermosphere from MIPAS (see, e.g. Funke et al. (2008b), Funke et al. (2008a)) and from Scisat-1/ACE-FTS (Sheese et al., 2016). Model-measurement studies by Semeniuk et al. (2008) attributed the source of this N<sub>2</sub>O to being most likely the reaction between NO<sub>2</sub> and N atoms produced by particle precipitation:



We note that photo-excitation and photolysis at 185 nm (vacuum UV) of NO or NO<sub>2</sub> mixtures in nitrogen, N<sub>2</sub>, or helium mixtures at 1 atm leads to N<sub>2</sub>O formation (Maric and Burrows, 1992). Both mechanisms explaining the production of N<sub>2</sub>O involve excited states of NO. Hence these pathways contribute to the loss of NO and potentially an additional daytime source of N<sub>2</sub>O in the upper atmosphere. N<sub>2</sub>O acts as an intermediate reservoir at high altitudes ...”

p3 l11-12: “NO is produced in dark conditions by particle precipitation at auroral latitudes, but is then depleted only by reacting with atomic nitrogen”. I don't understand this sentence. NO is produced by particle precipitation at any illumination condition. NO loss is mostly occurring at sunlit conditions (photolysis of NO and subsequent reaction R5).

We agree that in the way it is expressed, it is indeed misleading. We reordered this sentence to read:

“NO is produced by particle precipitation at auroral latitudes, but in dark conditions (without photolysis) it is depleted only by reacting with atomic nitrogen (reaction (R5)).”

p3 l22: The semi-empirical model of Funke et al. does not only cover the stratosphere but also a significant part of the mesosphere.

We added: “and mesosphere” after “stratosphere” to that sentence.

p4 l22: “We use two proxies to model the NO number densities, one accounting for the long-term eleven-year solar cycle and one accounting for the short term geomagnetic activity.” Isn't one of these proxies related to solar irradiance variations and the other one related to energetic particle precipitation? Both of them exhibit short- and longterm variability. . .

Our expression was indeed misleading and did not convey the meaning we intended (which is more accurately described by the reviewer's words). Thus, we changed the beginning of the paragraph to read:

"We use two proxies to model the NO number densities, one accounting for the solar irradiance variations and one accounting for the geomagnetic activity. Various proxies have been used or proposed to account for the solar irradiance induced variations in mesospheric–thermospheric NO, which are in particular related to the eleven-year solar cycle."

p5 l1: "questioned" seems too strong to me. Hendrickx et al. simply noticed "that the auroral electrojet index is a more suitable proxy".

We rephrased the sentence to read:

"However, Hendrickx et al. (2015) found that the auroral electrojet index (AE) (Davis and Sugiura, 1966) correlated better with SOFIE-derived NO concentrations (Hendrickx et al., 2015, 2017) (see also Sinnhuber et al., 2016)."

We further changed "matter of debate" to "matter of opinion" at the beginning of the paragraph in question.

p5 l11: The choice of geomagnetic latitude as coordinate deserves some further discussion: Although production by EPP is linked to geomagnetic latitudes, mesospheric NO distributions are mostly ruled by illumination and (to some extent) by dynamics, both resulting in NO distributions organized in geographic latitudes.

Geomagnetic latitudes were used by (Marsh et al., 2004), (Sinnhuber et al., 2016), and (Kiviranta et al., 2018), because particle-induced NO production is related to geomagnetic latitudes. We added the following note to Sect. 2.1:

"Note that mesospheric NO concentrations are related to geomagnetically as well as geographically based processes, but disentangling them is beyond the scope of the paper. Follow-up studies can build on the method presented here and study, for example, longitudinally resolved timeseries."

We then added a reference in the mentioned place.

"... function of the (geomagnetic, see Sect. 2.1) latitude  $\phi$ , ...

p5 Eq3: What is the rationale behind omitting the harmonic term in the non-linear model? By doing so, seasonal variations not related to EPP remain unconsidered. Or, in other words, the model is forced to attribute any seasonal variation to EPP. In the same line, shouldn't a life-time correction be considered also for the Ly- $\alpha$  part?

When there is strong UV-induced NO production, it is naturally depleted by photolysis (R3) or photoionization (R4) at the same time. The lifetime is therefore expected to be < 1 day. We tested a finite lifetime for the Lyman- $\alpha$  part, but found that this only increases the number of parameters without improving the fit quality.

We found that we could achieve similar or better fits to the data already without the harmonic terms in the non-linear model. We added the following text after Eq. (3):

"Although this approach shifts all seasonal variations to the AE index and thus attributes them to particle-induced effects, we found that the residual traces of particle-unrelated seasonal effects were minor compared to the overall improvement of the fit. Additional harmonic terms increase only the number of free parameters without substantially improving the fit further."

p6 l7: "accounts for the different lifetime at polar night compared to polar day. " This could be phrased in a more general way, i.e., ". . .during winter and summer".

We agree with the reviewer and changed the sentence to end in the suggested way.

p10 I2: The vertical shape of the Ly-a response is intriguing: Why is this response peaking at 70-75 km while NO production due to XEUV should increase with altitude?

The Lyman- $\alpha$  index predominantly describes the 11-year solar cycle. At middle and low latitudes, the time-series themselves show a pronounced solar cycle variation at this altitude range, and they get “flatter” above 75 km until the solar cycle is visible again at around 88 and 90 km. We added the following note after that sentence:

“The penetration of Lyman- $\alpha$  radiation decreases with decreasing altitude as a result of scattering and absorption by air molecules. On the other hand the concentration of air decreases with altitude. At this stage we have not an unambiguous explanation of this behaviour, but it may be related to reaction pathways as laid out by (Pendleton et al., 1983) which would relate the NO concentrations to the CO<sub>2</sub> and H<sub>2</sub>O (or OH, respectively) profiles.”

On a related issue we discovered that the stated N<sub>2</sub> dissociation energy is wrong. We therefore changed the statement below (R2) to:

“The dissociation energy of N<sub>2</sub> into ground state atoms N(<sup>4</sup>S) is about 9.8 eV ( $\lambda \approx 127$  nm) (Frost et al., 1956; Heays et al., 2017; Hendrie, 1954). This energy together with the excitation energy to N(<sup>2</sup>D) is denoted by  $h\nu$  in (R1) and can be provided by a number of sources, most notably by auroral or photoelectrons as well as by soft solar X-rays.”

And we added “( $\lambda < 102$  nm)” to reaction (R1).

p11 I4: The larger amplitude of the NH annual lifetime variation is likely a result of the use of the geomagnetic latitude grid (this variation is smeared out in the SH due to the geomagnetic pole offset).

We agree with the reviewer and added the following statement:

“This difference could be linked to the geomagnetic latitudes which include a wider range of geographic latitudes in the Southern Hemisphere compared to the Northern Hemisphere. Therefore, the annual variation is less apparent in the Southern Hemisphere.”

p12, I4-11: Similarly, the smaller SH AE coefficients (and shorter lifetimes) are likely related to the choice of a geomagnetic grid.

This is discussed at the end of that paragraph and we added another possible explanation:

“A third possibility may be the exclusion of the Southern Atlantic Anomaly from the retrieval (Bender et al., 2013, 2017) where presumably the particle-induced impact on NO is largest.”

p13 I2: The AE coefficients do not represent a NO production rate, they simply represent the NO response to AE perturbations. Note that transport and mixing processes are not considered by the empirical model, the latter being most likely responsible for the increased polar AE response around 70 km due to accumulation effects during the winter.

It is true that the AE coefficients are not production rates, we added the following statement to explain the conversion better:

“The AE coefficient can be considered as an effective production rate modulated by all short-time ( $\ll$  1 day) processes. To roughly estimate this production rate, we divided the coefficient of the (daily) AE by 86400 s which follows the approach in (Sinnhuber et al., 2016). We find a maximum production rate of about  $1 \text{ cm}^{-3} \text{ nT}^{-1} \text{ s}^{-1}$  around 70–72 km.”

We also changed the Figs. 3, 5, and 6 to show the original coefficients instead of the converted “production rates”. We already include an accumulation effect by our finite lifetime approach, see Eq. (4).

p14 I8: Note that the annually varying finite lifetime is only considered for the EPP-related part of NO.

We changed the sentence to end:

“... using an annually varying finite lifetime for the particle-induced NO.”

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Bender, S., Sinnhuber, M., Burrows, J. P., Langowski, M., Funke, B. and López-Puertas, M.: Retrieval of nitric oxide in the mesosphere and lower thermosphere from SCIAMACHY limb spectra, *Atmos. Meas. Tech.*, 6(9), 2521–2531, doi:10.5194/amt-6-2521-2013, 2013.

Bender, S., Sinnhuber, M., Langowski, M. and Burrows, J. P.: Retrieval of nitric oxide in the mesosphere from SCIAMACHY nominal limb spectra, *Atmos. Meas. Tech.*, 10(1), 209–220, doi:10.5194/amt-10-209-2017, 2017.

Bermejo-Pantaleón, D., Funke, B., López-Puertas, M., García-Comas, M., Stiller, G. P., Clarmann, T. von, Linden, A., Grabowski, U., Höpfner, M., Kiefer, M., Glatthor, N., Kellmann, S. and Lu, G.: Global observations of thermospheric temperature and nitric oxide from mipas spectra at 5.3 m, *J. Geophys. Res.*, 116(A10), A10313, doi:10.1029/2011JA016752, 2011.

Davis, T. N. and Sugiura, M.: Auroral electrojet activity index AE and its universal time variations, *J. Geophys. Res.*, 71(3), 785–801, doi:10.1029/jz071i003p00785, 1966.

Frost, D. C., McDowell, C. A. and Bawn, C. E. H.: The dissociation energy of the nitrogen molecule, *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 236(1205), 278–284, doi:10.1098/rspa.1956.0135, 1956.

Funke, B., García-Comas, M., López-Puertas, M., Glatthor, N., Stiller, G. P., Clarmann, T. von, Semeniuk, K. and McConnell, J. C.: Enhancement of N<sub>2</sub>O during the octoberNovember 2003 solar proton events, *Atmos. Chem. Phys.*, 8(14), 3805–3815, doi:10.5194/acp-8-3805-2008, 2008a.

Funke, B., López-Puertas, M., García-Comas, M., Stiller, G. P., Clarmann, T. von and Glatthor, N.: Mesospheric N<sub>2</sub>O enhancements as observed by MIPAS on envisat during the polar winters in 20022004, *Atmos. Chem. Phys.*, 8(19), 5787–5800, doi:10.5194/acp-8-5787-2008, 2008b.

Funke, B., López-Puertas, M., Stiller, G. P., Versick, S. and Clarmann, T. von: A semi-empirical model for mesospheric and stratospheric NO<sub>y</sub> produced by energetic particle precipitation, *Atmos. Chem. Phys.*, 16, 8667–8693, doi:10.5194/acp-16-8667-2016, 2016.

Heays, A. N., Bosman, A. D. and Dishoeck, E. F. van: Photodissociation and photoionisation of atoms and molecules of astrophysical interest, *Astronomy & Astrophysics*, 602, A105, doi:10.1051/0004-6361/201628742, 2017.

Hendrickx, K., Megner, L., Gumbel, J., Siskind, D. E., Orsolini, Y. J., Tyssøy, H. N. and Hervig, M.: Observation of 27 day solar cycles in the production and mesospheric descent of EPP-produced NO, *J. Geophys. Res.*, 120(10), 8978–8988, doi:10.1002/2015JA021441, 2015.

Hendrickx, K., Megner, L., Marsh, D. R., Gumbel, J., Strandberg, R. and Martinsson, F.: Relative Importance of Nitric Oxide Physical Drivers in the Lower Thermosphere, *Geophys. Res. Lett.*, 44(19), 10, 081–10, 087, doi:10.1002/2017gl074786, 2017.

- Hendrie, J. M.: Dissociation energy of N<sub>2</sub>, *The Journal of Chemical Physics*, 22(9), 1503–1507, doi:10.1063/1.1740449, 1954.
- Kiviranta, J., Pérot, K., Eriksson, P. and Murtagh, D.: An empirical model of nitric oxide in the upper mesosphere and lower thermosphere based on 12 years of Odin SMR measurements, *Atmos. Chem. Phys.*, 18(18), 13393–13410, doi:10.5194/acp-18-13393-2018, 2018.
- Maric, D. and Burrows, J.: Formation of N<sub>2</sub>O in the photolysis/photoexcitation of NO, NO<sub>2</sub> and air, *J. Photochem. Photobiol., A*, 66(3), 291–312, doi:10.1016/1010-6030(92)80002-d, 1992.
- Marsh, D. R., Solomon, S. C. and Reynolds, A. E.: Empirical model of nitric oxide in the lower thermosphere, *J. Geophys. Res.*, 109(A7), A07301, doi:10.1029/2003JA010199, 2004.
- Matthes, K., Funke, B., Andersson, M. E., Barnard, L., Beer, J., Charbonneau, P., Clilverd, M. A., Wit, T. D. de, Haberleiter, M., Hendry, A., Jackman, C. H., Kretschmar, M., Kruschke, T., Kunze, M., Langematz, U., Marsh, D. R., Maycock, A. C., Misios, S., Rodger, C. J., Scaife, A. A., Seppälä, A., Shangguan, M., Sinnhuber, M., Tourpali, K., Usoskin, I., Kamp, M. van de, Verronen, P. T. and Versick, S.: Solar forcing for CMIP6 (v3.2), *Geoscientific Model Development*, 10, 2247–2302, doi:10.5194/gmd-10-2247-2017, 2017.
- Orsolini, Y. J., Limpasuvan, V., Pérot, K., Espy, P., Hibbins, R., Lossow, S., Raaholt Larsson, K. and Murtagh, D.: Modelling the descent of nitric oxide during the elevated stratopause event of January 2013, *J. Atmos. Sol. Terr. Phys.*, 155, 50–61, doi:10.1016/j.jastp.2017.01.006, 2017.
- Pendleton, W., Erman, P., Larsson, M. and Witt, G.: Observation of strong NO gamma-band radiation induced in thin n<sub>2</sub>-CO<sub>2</sub> and n<sub>2</sub>-h<sub>2</sub>O targets by electron impact and its possible relation to the auroral chemistry of NO, *Physica Scripta*, 28(5), 532–538, doi:10.1088/0031-8949/28/5/005, 1983.
- Pérot, K., Urban, J. and Murtagh, D. P.: Unusually strong nitric oxide descent in the Arctic middle atmosphere in early 2013 as observed by Odin/SMR, *Atmos. Chem. Phys.*, 14(15), 8009–8015, doi:10.5194/acp-14-8009-2014, 2014.
- Semeniuk, K., McConnell, J. C., Jin, J. J., Jarosz, J. R., Boone, C. D. and Bernath, P. F.: N<sub>2</sub>O production by high energy auroral electron precipitation, *J. Geophys. Res.*, 113(D16), doi:10.1029/2007jd009690, 2008.
- Sheese, P. E., Walker, K. A., Boone, C. D., Bernath, P. F. and Funke, B.: Nitrous oxide in the atmosphere: First measurements of a lower thermospheric source, *Geophys. Res. Lett.*, 43(6), 2866–2872, doi:10.1002/2015gl067353, 2016.
- Sinnhuber, M., Friederich, F., Bender, S. and Burrows, J. P.: The response of mesospheric NO to geomagnetic forcing in 2002–2012 as seen by SCIAMACHY, *J. Geophys. Res.*, 121(4), 3603–3620, doi:10.1002/2015JA022284, 2016.