Revised submission of acp-2014-166 "Comparison of HONO budgets for two measurement heights at a field station within the Boreal Forest (SMEAR II – HUMPPA-COPEC-2010)".

Dear Editor,

Thank you for your patience and for agreeing on the requested extensions of deadlines to work on the manuscript. This allowed us to prepare a revised version of the manuscript, which we think addresses the concerns raised by the reviewers and which all coauthors agree on. We also finally managed to calculate the potential contribution of the "internal HONO source" from the reaction of HO_2-H_2O-complexes with NO_2 as requested by refree#2. A new paragraph describing the calculations and discussing the results has been added to section 3.3.1.
As requested we added a detailed description of the LOPAP instrument and all measures taken to avoid artefacts. We are pretty confident (there is never a 100% security in science) that the unknown source is not an instruments artefact for two reasons. First, the LOPAP has been tested for uncorrected interferences in many ways and the unknown source for HONO at lower ppt levels has been found by several instruments including DOAS and CIMS.

Besides some language corrections that are not marked, we marked all sentences, paragraphs and references that have been changed. Except for including a new paragraph concerning the HO_2 + NO_2 reaction the changes in the manuscript followed the argumentation given in the authors response to the referees.

Many thanks again to the anonymous referees for their valuable comments that helped to improve the manuscript.

Kind regards,

Matthias Sörgel and Robert Oswald on behalf of all co-authors

**Atmospheric
Chemistry
and Physics**
Discussions

Open Access

Interactive comment on **"Comparison of HONO budgets for two measurement heights at a field station within the boreal forest (SMEAR II – HUMPPA-COPEC 2010)"** *by* **R. Oswald et al.**

R. Oswald et al.

robert.oswald@mpic.de

General comments

"R. Oswald et al., 2014 has reported a background HONO measurement at both 1 m above ground surface and 2m above forest canopy. HONO budget features low contribution of other processes except for photolysis of HONO and unknown sources in background HONO chemistry. The gradient and diurnal profile of HONO may infer something we don't know yet. Overall, the introduction is in detail and accurate. The dataset is valuable and the analysis is reasonable. Thus I recommend publication in

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

ACP although several weakness that will be discussed in specific comments."

We thank referee #1 for the positive evaluation of our paper and his valuable comments.
Specific Comments

"1. In line 26 page 7828 and in line 25 in page 7837, the author mentioned drying ground surface would be a source of HONO and the change of temperature of soil surface in the morning. It was inferred from early morning to noontime with the temperature increasing, drying soil surface would be a HONO source. In fact, not only soil surface, leaf surface may also be a source due to drying of dew in the morning, see He Y et al., 2006. Both higher NO concentration in the early morning in figure 1 and smaller ratio of Lphot/Punknown in the morning than the noontime, see line 4 page 7840 and figure 5 indicate HONO and NO emission in the morning. Intensively increasing of HONO concentration in figure 1 after "the short and strong rain (line 15 page 7833)" before sun rise and when NOx concentration were still low also infers a emission source. Soil emission experiment reported in this manuscript may use disturbed soil and hence cannot represent the reactivity of the nitrous acid rich soil surface due to deposition in the night. Failure to account for this term potentially jeopardizes the reliability of correlation analysis in Figure 6, especially for the data point from the morning."

The referee raises an interesting point: There are potentially other processes of HONO reemission that follow the temperature increase in the mooring than just from equilibrium between soil nitrite and HONO or microbiological formation in soil. We added the two processes of dew evaporation (He et al., 2006) and reemission of deposited HONO (VandenBoer et al., 2013) to the text. The referee mentioned reasonable arguments for a NOx independent HONO source. Regarding the correlation in Fig. 6 there seems to be no systematic deviation from the correlation for low J(NO2) values = morning and evening. Furthermore, as low J(NO2) values represent morning and evening the values should split in these two regimes, which is not evident from Fig. 6.

"2. In line 27 and 28 page 7835, the author cited Wong et al., 2013:" the contribution of vertical transport to surface loss of HONO was estimated to be about 50 to 60%", yet no mention of how to calculate this term in equation (8) and no such term in Fig.5."

Wong et al. (2013) used a modelling approach to infer these values. From our measurements we were not able to perform a proper estimate of this contribution. Furthermore, none of the budget studies based on field measurements published so far has taken this term into account. A detailed discussion of the possible contribution of the vertical transport without further investigation and measurements is very speculative. Therefore, we prefer not to include more details about this topic in the present manuscript.

"3. In line 25 page 7840, the author mentioned:" the wild fire pollution plumes transported from Russia". The author should point out which data point came from this particular event in figure 1 and figure 8, also what is the intention and implication to involve the data point in HONO chemistry analysis in a forest. I would also suggest to point out other special events if any in figure 1 and also in result section."

We added the classifications of "normal boreal", "stressed boreal" and "transported pollution (Russian wildfire) according to Nölscher et al. (2012) to Figs. 1 and 8.

"4. In line 7 page 7839, Zhou et al., 2003, 2011 didn't intend to recommend an enhancement factor of 43. Thus it is improper to rule out absorbed HNO3 as a HONO precursor with the data the author presented."

We did not rule out HNO3 photolysis as a source of HONO (see also p 7841, L19 ff.). Nevertheless, such a strong enhancement (here a required factor of about 400) is very unlikely as it would substantially shift the NOx cycling by reducing the lifetime of deposited HNO3 to 1/400 of its lifetime in the gas phase. For a better understanding, we modified line 7 on page 7839.

References

He, Y., Zhou, X., Hou, J., Gao, H., and Bertman, S. B.: Importance of dew in controlling the air-surface exchange of HONO in rural forested environments, Geophysical Research Letters, 33, L02813, 10.1029/2005GL024348, 2006.

Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., de Arellano, J. V. G., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, Atmospheric Chemistry and Physics, 12, 8257-8270, 10.5194/acp-12-8257-2012, 2012.

VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., de Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M., and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, Journal of Geophysical Research: Atmospheres, 118, 10,155-110,171, 10.1002/jgrd.50721, 2013.

Wong, K. W., Tsai, C., Lefer, B., Grossberg, N., and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, Atmos. Chem. Phys., 13, 3587-3601, 10.5194/acp-13-3587-2013, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7823, 2014.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

**Atmospheric
Chemistry
and Physics**
Discussions

Interactive comment on "**Comparison of HONO budgets for two measurement heights at a field station within the boreal forest (SMEAR II – HUMPPA-COPEC 2010)**" *by* R. Oswald et al.

R. Oswald et al.

robert.oswald@mpic.de

General comments "This paper presents measurements of HONO and budgets for its daytime production and loss at two measurement heights during the SMEAR II campaign, a site in the boreal forest in Hyytiala. Like several other recent field studies, results show that the daytime budget for HONO is not balanced, with no clearly identified source able to explain the presence of measurable HONO, a species that undergoes rapid photolytic loss. The authors consider and attempt to quantify several potential HONO sources that could address this imbalance. These include the gas phase reaction of OH + NO, the heterogeneous reaction of NO_2 with water leading

to disproportionation to HONO + HNO3, photolysis of nitrophenols, photosensitized heterogeneous uptake of NO2 to soils, emission of HONO from soil and photolysis of surface absorbed HNO3. The work is comprehensive, since it nicely considers all of these sources. However, the authors also show that none of these sources can explain the observations, and that the apparent HONO source is correlated most convincingly with its photolytic loss rather than with any other single parameter possibly related to the above sources. The presentation and discussion of the HONO photochemistry is well done. However, the authors fail to consider or allow the potentially most obvious explanation of these observations, which would be a small interference on the Lopap instrument that is unrelated to HONO itself, or from uncertainty in the zero level of the instrument. Such an interference or zero uncertainty would produce an apparent budget that would correlate perfectly with the photolytic loss for HONO. The authors should state clearly why they believe that the HONO measurements are reliable enough at the several tens of parts per trillion level. I recommend publication of this manuscript only with the addition of such a section or with some additional detail added to the experimental section, since a low-level interference or offset would clearly provide the simplest explanation of the observations. The paper also does not consider the implications of the measurements for either the HOx or the NOx budgets. How large a contribution do the observed HONO levels make to either? The recent Li et al. paper in Science (2014) suggests that HONO observations cannot be reconciled with HOx or NOx budgets unless the HONO source is itself derived from something that consumes both HOx and NOx. Can the authors make quantitative comparisons to these budgets and state how this constraint might affect each of the source terms they consider? "

We thank referee #2 for the detailed evaluation of our paper and the valuable comments that will help to further improve the manuscript.

We agree with the referee that the accuracy of the HONO measurements is crucial for determining the budget. The experimental section has been extended to discuss

the reliability of the LOPAP at the lower ppt range (see detailed comments below). We are confident that these values are not an instrument artefact as HONO daytime values in the lower ppt range were also observed by other techniques (see manuscript p 7841, L1). The study from Li et al. in Science (2014) was not yet published when we submitted this paper. We will briefly discuss the implications of this "new HONO source" for the budget at our site in the revised version of the paper. However, a detailed investigation and comparison of HOx and NOx budgets is out of the scope for this study (for details see Hens et al., 2013).

Specific comments

"1. Page 7827, line 2: Phrase "less important" is confusing here, since reactions R2 and R3 are not in competition. Clearer would be "the flux (or mass) through this reaction is smaller," or something to that effect."

We clarified this sentence to:" ...has less influence on HONO cycling than (R2) even with...as the turnover is low and constitutes…"

"2. Page 7828, equation (3). For completeness, best to specify units. Also, is the upper limit given here due to just the absorption cross section of nitrophenols relative to NO2, or due to the absorption cross section and a quantum yield for HONO?"

We specified the units. The text reads now as follows:" …it is possible to estimate the photolysis frequency (in s-1) by an upper limit…." The upper limit approach is based on measured photolysis rates that were converted to photolysis frequencies (Bejan et al., 2006). They are not based on absorption cross sections and quantum yields. The factor of 2.5 *10^-3 arises from the ratio of J(o-NP => HONO)/J(NO2) measured by Bejan et al. (2006) and the relation to J(HONO) from a factor of 0.175 of J(HONO)/J(NO2) as derived by Trebs et al. (2009). We clarified the text accordingly.

"3. Page 7831, experimental section. The experimental section is very brief and relies upon a reference to an earlier paper to describe the HONO measurements. In that

earlier paper, the two LOPAP instruments were compared using identical 50cm-long inlets. Are the same inlets used here? If not, this paper should note the inlet length and residence time. Also, the paper should discuss the instrument diagnostics that were performed. Were there any efforts to calibrate or zero the instruments at the field site? Power disruptions are used to explain why simultaneous measurements were available only 30% of the campaign. How long did it take to restart an instrument after a power disruption? Since daytime HONO levels are much higher than can be understood, the authors must do more to justify that their measurements are free from artifacts at 20 ppt level. It appears that HONO is always well above zero (Fig 1). How well is the instrumental background understood? Also, how was J(HONO) measured?"

No inlet lines were used. Also in the study of Sörgel et al. (2011b) no inlet lines have been used for the intercomparison. We clarified the text accordingly by introducing: "Artefacts due to wall reactions are minimized in the LOPAP by using an external sampling unit where the derivatization takes place, instead of using inlet lines. The LOPAP uses two stripping coils in series. Hence, potential interferences are accounted for by quantitatively sampling of HONO in the first coil by a fast and specific reaction (Heland et al., 2001;Kleffmann et al., 2002). All interferences are assumed to react in the same way in both coils and, therefore, the HONO signal can be corrected. The zero level of the instrument was checked automatically several times (every 4 hours for 30 min.) per day using purified air. Consequently, any diurnal fluctuation of the background signal is subtracted from the HONO signal. Potential interferences of the LOPAP instrument have been discussed in several studies including those cited in the manuscript (Heland et al., 2001;Kleffmann et al., 2002). There is only one study (Kleffmann and Wiesen, 2008) that studied interferences for HONO measurements with the LOPAP in the low ppt range and proved its reliability. Furthermore, Sörgel et al. (2011a) measured values around the detection limit ($\sim$ 2 ppt) in clean marine background air, thus in clean ambient air no background HONO has been observed. In this study, values reached the detection limit after a rain event (see manuscript line 15, page 7833). Furthermore, daytime values in the lower ppt range but well above the PSS were measured by dif-

ferent techniques (see manuscript page 7841). J(HONO) was calculated according to Trebs et al. (2009) from J(NO2) measurements by a filter radiometer.

"4. Page 7831, line 25: What does "reasonable agreement" mean? Please give a quantitative comparison of the two OH instruments."

For more detail on OH LIF and OH CIMS please refer to Hens et al. (2013).

"5. Page 7832, Results section: More discussion of the NO2 levels is needed. They are shown in Fig1, and one day with low NO2 levels is mentioned. But many studies report the relationship between HONO and NO2, and it would be helpful here to discuss the NO2 levels and the relationship to HONO. Also, NO2 conversion to HONO on activated surfaces are proposed as a possible HONO source. Could this occur in the instruments or inlets?"

As described above, no inlet lines were used. A short $\sim$ 1.5 cm radiation shielded glass inlet is the only instrument surface to which the sampling air is exposed to before HONO is stripped in the first coil. It is not exposed to direct sunlight and, therefore, fast photochemical reactions can be ruled out. The slower heterogeneous reactions of NO2 can be ruled out as the residence time is in the milli-second range. The NO2 interference in the stripping coil has been minimized by using a highly acidic (1 mol l-1 HCl) sampling solution and it was shown, that this minimized interference is efficiently corrected for by the two channel design (Heland et al., 2001;Kleffmann et al., 2002). If HONO values would arise from NO2 interference they should be directly correlated to NO2, which was not the case. Instead of discussing the NO2 levels in relation to HONO we calculated HONO formation from (dark) heterogeneous NO2 conversion during the night (Phet, Fig.5) according to the generally accepted approach of Alicke et al. (2002). This source did not play a role for daytime HONO formation. To clarify this we added some discussion on Phet to the results section. Furthermore, in section 3.3.1 we discuss the light induced NO2 conversion as potential HONO source and provide some information about NO2 values.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

"6. Page 7834: dHONO/dt is not defined. What is the time step here? It appears to be the 1 hour time step between averaged observations in figure 5. But photolytic loss of HONO is quite a bit faster than this time step, so in reality the better form of this equation is to simply set dHONO/dt to zero and just solve for the difference between sources and sinks? It seems in reality this is what the authors have done. The need for explicit inclusion of dHONO/dt for slow observations is not clear."

Indeed, dHONO/dt is defined in eq. 7. Its value equals zero only if the sources and sinks are equal. As HONO values change during the course of the day there must be a (local) imbalance of the sources and sinks and, thus, dHONO/dt has to be taken into account otherwise sources or sinks would be over/underestimated. The referee is right that HONO lifetime during midday is much lower that the averaging interval (given by other data), but to take into account the "real loss" by photolysis during daytime we have to account for a change in the HONO concentration over that time (i.e. dHONO/dt).

"7. Page 7835, last paragraph. The HONO observations presented here show at best only a modest vertical gradient. It seems unreasonable to apply a 50-60% contribution of vertical transport to HONO loss? Perhaps the argument of this paragraph could be clarified."

In case a ground source and photolytic loss exists within the boundary layer, the argument has to be reversed. Without considerable upward transport of HONO (surface loss), substantial gradients would exist. This means a small gradient indicates fast vertical transport (c.f. (Sörgel et al., 2011b)). Even a light dependent volume source would result in visible gradients without vertical mixing due to the shading of the canopy. As already pointed out in the reply to referee 1, we believe that a qualitative discussion of this topic without further measurements is highly speculative and we prefer not to include it in the revised version.

"8. Page 7837, lines 14-21: A humic acid soil source would likely lead to a gradient in HONO, with larger values at 1 m than 24 m, correct? Are the modest gradients

and their diurnal variation consistent with or contrary to this source? Section 3.3.3, HNO3 photolysis: Is the use of the HNO3 surface loading from Zhou et al. likely to be applicable to the SMEAR environment? A short comparison of the sites with some justification is warranted. As in the comment above, would surface HNO3 lead to an observed gradient in HONO? Can the height resolved measurements and their diurnal variation provide any insight?"

Unfortunately, only gradients without fluxes do not provide detailed information into the vertical source or sink distribution. Hence, from the gradients alone we cannot favor one or the other source. Certainly, there would be more humic acids at the ground, but there is also less radiation available (see Fig. 1), which is essential to accelerate this reaction to levels comparable to daytime HONO formation (Stemmler et al., 2006). We believe that the values of Zhou et al. (2011) can serve as a best guess as the SMEAR II site as well as the PROPHET site where Zhou et al. (2011) measured are rural forested sites. Furthermore, Zhou et al. (2011) report their values to be close to one monolayer coverage, thus we do not expect much higher values for the SMEAR II site that are effective for photochemistry. In the revised version we will provide a more detailed intercomparison of the sites in the text. Additionally, the height resolved values do not provide much insight as during the most intensive photochemistry vertical transport is also maximal (ff. (Sörgel et al., 2011a)), which (in a well-mixed situation) on the other hand is a prerequisite to apply the budget method.

Figures: "Fig 1 is difficult to read. Some of the panels have two red traces, and I can't know which trace goes to which label. Please use 3 colors for 3 traces, and much larger axis labels. Both concentrations and mixing ratios are used to describe abundance of a single compound, which makes it hard to compare figures. Please choose just one unit for each compound."

As suggested by the referee in cases of two red colored traces in Figure 1 we changed one trace to green color. Also the axis labels were enlarged. We used the unit ppt for NO and HONO in Figure 1 for an easy comparison of values with other publications.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The change to molec. cm-3 in the following figures is due to the general use of this unit for the calculation of reaction kinetics and use of reaction rate constants. For best comparison with other publications there is no other choice than changing the unit.

References

Alicke, B., Platt, U., and Stutz, J.: Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, J. Geophys. Res., 107, LOP9-1-LOP9-LOP9-17, 10.1029/2000jd000075, 2002.

Bejan, I., Abd El Aal, Y., Barnes, I., Benter, T., Bohn, B., Wiesen, P., and Kleffmann, J.: The photolysis of ortho-nitrophenols: a new gas phase source of HONO, Physical Chemistry Chemical Physics, 8, 2028-2035, 2006.

Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, Environmental Science & Technology, 35, 3207-3212, 10.1021/es000303t, 2001.

Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A. C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of HOx radicals in a boreal forest, Atmos. Chem. Phys. Discuss., 13, 28561-28629, 10.5194/acpd-13-28561-2013, 2013.

Kleffmann, J., Heland, J., Kurtenbach, R., Lörzer, J., and Wiesen, P.: A new instrument (LOPAP) for the detection of nitrous acid (HONO), Environmental Science and Pollution Research, 48-54, 2002. Kleffmann, J., and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions, Atmos. Chem. Phys. Discuss., 8, 3497-3523, 10.5194/acpd-8-3497-2008, 2008.

Sörgel, M., Regelin, E., Bozem, H., Diesch, J. M., Drewnick, F., Fischer, H., Harder,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

H., Held, A., Hosaynali-Beygi, Z., Martinez, M., and Zetzsch, C.: Quantification of the unknown HONO daytime source and its relation to NO2, Atmospheric Chemistry and Physics, 11, 10433-10447, 10.5194/acp-11-10433-2011, 2011a.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, Atmospheric Chemistry and Physics, 11, 841-855, 10.5194/acp-11-841-2011, 2011b. Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195-198, 2006.

Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Königstedt, R., Meixner, F. X., Fan, S., and Andreae, M. O.: Relationship between the NO2 photolysis frequency and the solar global irradiance, Atmospheric Measurement Techniques, 2, 725-739, 2009.

Zhou, X. L., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nat. Geosci., 4, 440-443, 10.1038/ngeo1164, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7823, 2014.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

1 **Comparison of HONO budgets for two measurement**

2 **heights at a field station within the Boreal Forest (SMEAR II**

3 **– HUMPPA-COPEC-2010)**

4

5 **R. Oswald[1,2], M. Ermel[1,2], K. Hens[3], A. Novelli[3], H. G. Ouwersloot[3,4], P.**

6 **Paasonen[5], T. Petäjä[5], M. Sipilä[5], P. Keronen[5], J. Bäck[6], R. Königstedt[3], Z.**

7 **Hosaynali Beygi[3], H. Fischer[3], B. Bohn[7], D. Kubistin[3,8], H. Harder[3], M. Martinez[3],**

8 **J. Williams[3],T. Hoffmann[2], I. Trebs[1*], and M. Sörgel[1]**

9 [1] Biogeochemistry Department, Max Planck Institute for Chemistry, P.O. Box 3060, 55020

10 Mainz, Germany

11 [2] Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz,

12 55128 Mainz, Germany

13 [3] Airchemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

14 [4] Meteorology and Air Quality, Wageningen University, Wageningen, The Netherlands

15 [5] Department of Physics, P.O. Box 64. 00014 University of Helsinki, Finland

16 [6] Department of Forest Sciences, P.O. Box 27, 00014 University of Helsinki, Finland

17 [7] Institut für Energie- und Klimaforschung IEK-8: Troposphäre, Forschungszentrum Jülich

18 GmbH, 52428 Jülich, Germany

19 [8] University of Wollongong, School of Chemistry, Wollongong, Australia

20 [*] now at: Centre de Recherche Public - Gabriel Lippmann, Department Environment and

21 Agro-biotechnologies, 41 rue du Brill, L-4422 Belvaux, Luxembourg

22

23 Correspondence to: m.soergel@mpic.de

1 **Abstract**

2 Atmospheric concentrations of nitrous acid (HONO), one of the major precursors of the

3 hydroxyl radical (OH) in the troposphere, significantly exceed the values predicted by the

4 assumption of a photostationary state (PSS) during daytime. Therefore, additional sources of

5 HONO were intensively investigated in the last decades. This study presents budget

6 calculations of HONO based on simultaneous measurements of all relevant species including

7 HONO and OH at two different measurement heights, i.e. 1 m above ground and about 2 to 3

8 m above canopy (24 m above ground), conducted in a Boreal forest environment. We

9 observed mean HONO concentrations during daytime of about 6.5×10^8 molecules cm^{-3} (26

10 ppt), more than twenty times higher than expected from the PSS, 0.2×10^8 molecules cm^{-3} (1

11 ppt). To close the budgets at both heights, a strong additional source term during daytime is

12 required. This unidentified source is maximal at noon (up to 1.1×10^6 molecules $cm^{-3} s^{-1}$, 160

13 ppt h^{-1}) and in general up to 2.3 times stronger above the canopy than close to the ground. The

14 insignificance of known gas phase reactions and also other processes like dry deposition or

15 advection, compared to the photolytic decomposition of HONO at this measurement site was

16 an ideal prerequisite to study possible correlations of this unknown term to proposed HONO

17 sources. But neither the proposed emissions from soils nor the proposed photolysis of

18 adsorbed HNO_3 contributed substantially to the unknown source. However, the unknown

19 source was found to be perfectly correlated to the unbalanced photolytic loss of HONO.

20

21 **1 Introduction**

22 Since the first unequivocal detection of HONO in the atmosphere by Perner and Platt (1979),

23 its formation and fate as well as its contribution to primary OH production has been

24 intensively studied (Lammel and Cape, 1996; Kleffmann, 2007). Recently, the importance of

25 HONO in atmospheric chemistry and its implications has been demonstrated using a global

26 chemistry transport model (Elshorbany et al., 2012). While the fate of HONO is mainly

27 determined by the photolytic decomposition producing OH, the major uncertainty in

28 modelling studies results from the lack of understanding the HONO formation pathways.

29 Budget calculations of the postulated sources and sinks (Kleffmann et al., 2005; Su et al.,

30 2008b; Sörgel et al., 2011a) have usually been used to quantify the magnitude of the missing

31 source term. Only a few source estimates derived from flux measurements have been

32 published up to now (Zhang et al., 2012; Zhou et al., 2011; Ren et al., 2011). The current

status of HONO formation and loss pathways, important for atmospheric chemistry is as follows.

The major sink during daytime for HONO is the homolytic cleavage of the O-N single bond by radiation ($\lambda < 400$ nm), determined by the photolysis frequency, J(HONO).

$$HONO \xrightarrow{h\nu} OH + NO \tag{R1}$$

Since OH is produced, this reaction is of primary importance to atmospheric photochemistry. J(HONO) shows a similar wavelength dependency as the photolysis frequency of nitrogen dioxide (NO_2), $J(NO_2)$ (Kraus and Hofzumahaus, 1998). Therefore J(HONO) can be linked to $J(NO_2)$ by using the approach of Trebs et al. (2009):

$$J(HONO) = 0.17 \text{ x } J(NO_2) \tag{1}$$

The back reaction of (R1) in presence of a third body can reform HONO with a rate constant (k_2 at 298 K and 1013 hPa) of $(7.4 \pm 1.3) \text{ x } 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (reaction (R2)) (Sander et al., 2011).

$$OH + NO \xrightarrow{M} HONO \tag{R2}$$

While the gas phase reaction of OH with NO forms HONO, OH may also react with HONO and reform NO_x.

$$HONO + OH \rightarrow NO_2 + H_2O \tag{R3}$$

Since concentrations of HONO and OH are generally much lower than those of NO, reaction (R3) has less influence on HONO cycling than reaction (R2), although the reaction rate constant (k_3 at 298 K and 1013 hPa) of about $6.0 \text{ x } 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ is similar (Atkinson et al., 2004). Hence, the turnover is low and contributes typically less than 5 % to the total HONO loss (Su et al., 2008b; Sörgel et al., 2011a).

A surface reaction of NO_2 and H_2O was suggested as another formation pathway for HONO. Finlayson-Pitts et al. (2003) proposed a mechanism, whereby NO_2 is dimerized and then dissolved in a humid surface film. The formed N_2O_4 rearranges into the mixed anhydride of nitrous acid and nitric acid ($ONONO_2$), which rapidly dissolves into HONO and nitrate.

$$2NO_2(g) + H_2O(l) \rightarrow HONO(g) + H^+(aq) + NO_3^-(aq) \tag{R4}$$
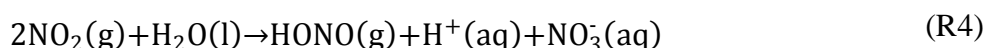
1 Yabushita et al. (2009) and De Jesus Medeiros and Pimentel (2011) further investigated the
2 mechanism with focus on the NO_2 uptake and the kinetics of the initial hydrolysis. The
3 reaction rate constant of reaction (R4) is difficult to determine in the field, but can be
4 estimated with the approach of Alicke et al. (2002).

$$k_4^{dark} = \frac{[HONO]_{max} - [HONO]_{sunset}}{(t_{max} - t_{sunset}) \times \overline{[NO_2]_{t_{sunset}}^{t_{max}}}} \tag{2}$$

5 After sunset the concentration of HONO, $[HONO]_{sunset}$, increases and reaches a maximum,
6 $[HONO]_{max}$. The difference between $[HONO]_{max}$ and $[HONO]_{sunset}$ divided by the product of
7 the elapsed time (t_{max}-t_{sunset}) and the average NO_2 concentration during that time, $\overline{[NO_2]_{t_{sunset}}^{t_{max}}}$,
8 determines the rate of heterogeneous HONO formation during the night. The reaction rates
9 found for nighttime conversion range from 0.4 (Kleffmann et al., 2003) to 2.0 ppb(HONO) x
10 ppb$(NO_2)^{-1}$ x h^{-1} (Sörgel et al., 2011a). This approach is only valid, if the heterogeneous dark
11 reaction (R4) is the dominant source of HONO during night.

12 Beside the dark reaction of NO_2, ortho-nitrophenols, o-NPs, can photolytically decompose to
13 form HONO as a side product (Bejan et al., 2006).

$$\text{o-NPs} \xrightarrow{h\nu} [products]^* + HONO \tag{R5}$$

14 The authors propose parts of the reaction mechanism, but since they could not measure the
15 main products, the exact and complete mechanism is not yet clarified. It is further stated that
16 this source might be of primary interest for the atmosphere under urban conditions, where
17 possibly 1 ppb of o-NPs occurs. Since the o-NPs absorb light in a similar wavelength range as
18 NO_2, it is possible to estimate the photolysis frequency (in s^{-1}) of o-NPs (J(o-NPs)) based on
19 measured relative photolysis frequencies of HONO formation from o-NPs and that of NO_2
20 (Bejan et al., 2006). This approach gives an upper limit for HONO formation from o-NPs.
21 $J(NO_2)$ can be substituted by J(HONO) according to Eq. (1).

$$J(\text{o-NPs}) = 2.5 \times 10^{-3} \times J(NO_2) = 1.4 \times 10^{-2} \times J(HONO) \tag{3}$$

22 In addition to the reaction of NO_2 with surface adsorbed water (R4), Stemmler et al. (2006)
23 and (2007) found that a surface film or aerosol of humic acid (HA) can act as photosensitizer
24 when irradiated and reduces NO_2 to HONO.

$$HA \xrightarrow{h\nu} A^{red} + X^{ox} \tag{R6}$$

$$A^{red} + X^{ox} \rightarrow HA' \tag{R7}$$

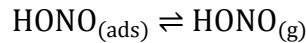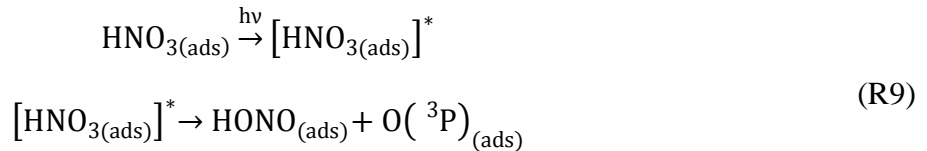$$A^{red} + NO_2 \rightarrow HA'' + HONO \tag{R8}$$

HA naturally occurs in the environment for example in soil. Hence, soil might act as a source for HONO under irradiation in the UV and exposure to NO_2 (Stemmler et al., 2006). Other reactants than A^{red} in reaction (R8) might also be reductive. E.g. fresh soot particles are supposed to reduce NO_2 and form HONO. This source is only important for high NO_2 concentrations and environments with freshly emitted soot (Aubin and Abbatt, 2007; Monge et al., 2010).

It was shown by several studies (Kubota and Asami, 1985; Twigg et al., 2011; Su et al., 2011; Oswald et al., 2013) that soils can emit HONO. Decreasing soil water content and, hence, drying out of soil leads to an increase in soil aeration with emission of trace gases, namely N_2O, NO and HONO. Due to the complexity of soil emission fluxes, depending on biological, physical and chemical processes as well as on soil properties, it is not straight forward to calculate the source strength, although observed NO emissions might serve as a proxy for HONO emission fluxes (Oswald et al., 2013). Furthermore, the exchange of HONO between the soil and atmosphere may be influenced by accumulation of deposited HONO at the soil surface and subsequent reemission during day (VandenBoer et al., 2013). This may lead to enhanced emission of HONO compared to performed laboratory soil studies. Similar drying leaf surfaces can release HONO from evaporating dew (He et al., 2006), which constitutes another process related to drying surfaces.

Surface adsorbed nitric acid $HNO_{3(ads)}$ that is either deposited or directly formed during the reaction cascade of (R4) was proposed to be photolytically sensitive and might decompose to HONO in the UV (Zhou et al., 2011).

$$HNO_{3(ads)} \xrightarrow{h\nu} \left[HNO_{3(ads)}\right]^*$$

$$\left[HNO_{3(ads)}\right]^* \rightarrow HONO_{(ads)} + O\left(^3P\right)_{(ads)} \tag{R9}$$

$$HONO_{(ads)} \rightleftharpoons HONO_{(g)}$$

The production of HONO by photolysis of $HNO_{3(ads)}$ depends on the physicochemical state of the surface. While for dry surfaces (relative humidity (RH) = 0%) NO_x is the major product, relative humidity of about 20 % suffices to increase the HONO yield (Zhou et al., 2003).

According to Goodman et al. (2001), at 20 % RH at least a monolayer of water present should be on the surface. Zhou et al. (2003) further propose that $NO_{2(ads)}$ formed during the photolysis of $HNO_{3(ads)}$ may also react further via reaction (R4), which not only forms HONO, but also recovers parts of HNO_3. Later on, Zhou et al. (2011) suggested that the formed NO_2 is reduced to HONO via the mechanism of reaction (R6) and (R8) proposed by Stemmler et al. (2006). However, the rate of HONO formation depends on the amount of HNO_3 available on irradiated surfaces and the photolysis frequency of HNO_3, $J(HNO_3)$, which is enhanced by adsorption to surface compared to gas phase photolysis (Zhu et al., 2008; Zhu et al., 2010). Depending on the type of surface the enhancement factor varies; Zhou et al. (2003) found an enhancement of about 2 orders of magnitude by HNO_3 adsorption on borosilicate glass (see also Ramazan et al., 2004), while Baergen and Donaldson (2013) calculated an enhancement of about 4 orders of magnitude by HNO_3 adsorbed to grime.

Other loss terms than reactions (R1) and (R3) include the dry and wet deposition of HONO. The dry deposition of HONO depends on the ambient mixing ratio of HONO, on turbulent mixing within the planetary boundary layer and the ability of terrestrial surfaces to take up HONO. With a Henry coefficient of 49 M atm^{-1} (Park and Lee, 1988), wet deposition of HONO is quite efficient especially for neutral to alkaline solutions (effective Henry coefficient). Mixing ratios of HONO strongly decrease after a rain events (Sörgel et al., 2011b).

Assuming only the known gas phase reactions R1 to R3 contribute to the HONO formation, a photostationary state should be established (Kleffmann et al., 2005),

$$\frac{d[HONO]_{PSS}}{dt} = k_2[NO][OH] - J(HONO)[HONO]_{PSS} - k_3[OH][HONO]_{PSS} = 0 \tag{4}$$

$$\Rightarrow \quad [HONO]_{PSS} = \frac{k_2[NO][OH]}{J(HONO) + k_3[OH]} \tag{5}$$

This equilibrium can only explain a minor portion of gas phase HONO observed at remote and rural sites (Kleffmann, 2007; Su et al., 2008b; Sörgel et al., 2011a; Wong et al., 2012), but may play an important role for measurement results obtained in urban areas (Lee et al., 2013). The budget calculations of Sörgel et al. (2011a) and Li et al. (2012) showed that including heterogeneous reactions of NO_2 (R4) only slightly improves the discrepancy between $[HONO]_{PSS}$ and measured HONO mixing ratios.

1 In this study, we present the results of the field campaign HUMPPA-COPEC 2010 (Hyytiälä

2 United Measurement of Photochemistry and Particles in Air – Comprehensive Organic

3 Precursor Emission and Concentration study) related to HONO chemistry and we provide a

4 detailed overview of its sources and sinks using a budget calculation for two measurement

5 heights, i.e. below and above a boreal forest canopy. We explicitly analyse additional source

6 terms, such as HONO emission by soil and the formation of HONO by photolysis of

7 $HNO_{3(ads)}$.

8

2 Experimental

10 The HUMPPA-COPEC-2010 was a comprehensively instrumented intensive field

11 measurement campaign, performed from 12 July until 12 August at the SMEAR II site

12 (Station for Measuring Ecosystem-Atmosphere Relation; 61.846°N, 24.295°E) located in the

13 Boreal forest in Hyytiälä (Williams et al., 2011).

14 HONO was measured using two Long Path Absorption Photometer instruments (LOPAP,

15 QUMA Elektronik & Analytik, Wuppertal, Germany). A detailed description of the

16 instrument has been given by Kleffmann et al. (2002) and Heland et al. (2001). Briefly, an

17 acidic solution of sulfanilamide is used to sample HONO with a stripping coil. HONO is

18 transformed rapidly into a diazonium salt, the precursor of diazotation, carried out in

19 sequence. The concentration of the azo dye formed is equivalent to the concentration of

20 HONO in the sampled air and is measured by a VIS-photometer. Artefacts due to wall

21 reactions are minimized in the LOPAP by using an external sampling unit where the

22 derivatization takes place, instead of using inlet lines. A short (L=1.5 cm) radiation shielded

23 glass inlet is the only instrument surface to which the sampling air is exposed to before

24 HONO is stripped in the first coil. The LOPAP uses two stripping coils in series. Hence,

25 potential interferences are accounted for by quantitatively sampling of HONO in the first coil

26 using a fast and specific reaction (Kleffmann et al., 2002; Heland et al., 2001). All

27 interferences are assumed to react in the same way in both coils and, therefore, the HONO

28 detection can be corrected using the measured "artefact HONO" in the second coil. The

29 background signal of the instrument was checked automatically for 30 minutes every four

30 hours using purified air. Consequently, all diurnal fluctuations of noise is monitored and

31 considered in the evaluation of the results. The comparison of both LOPAP instruments used

32 in this study has been described in detail by Sörgel et al. (2011b) and showed a good

1 agreement, within 12 % under dry conditions (no rain or fog). The inlets of the two

2 instruments were positioned at about 1 m and 24 m above ground (canopy top height 20 to 21

3 m). Both instruments were operated with a response time of below 10 min and lower limit of

4 detection ranging from 0.2 to 1.3 ppt during the campaign.

5 A laser induced fluorescence (LIF) instrument to measure the atmospheric concentration of

6 the hydroxyl radical, OH, based on the fluorescence assay by gas expansion technique

7 (FAGE) (Hens et al., 2014; Novelli et al., 2014) measured OH above the canopy at a height of

8 about 24 m, while a chemical ionization mass spectrometer (CIMS; Petäjä et al., 2009)

9 measured OH near to the ground at about 1 m. Lower detection limits of LIF and CIMS were

10 about 9×10^5 molecules cm^{-3} and 5×10^4 molecules cm^{-3}, respectively. For a detailed

11 description we refer to (Hens et al., 2014).

12 NO and NO_x were monitored by high resolution and high sensitivity chemiluminescence

13 detectors, a TEI 42C TL (Thermo Fisher Scientific, US) with a limit of detection of about 0.1

14 ppb positioned at 4 m, and a modified (Hosaynali Beygi et al., 2011) CLD 790 SR with a

15 detection limit of about 16 ppt (ECO-Physics, Switzerland) positioned at 24 m above ground.

16 Both instruments use a blue light converter for efficient and selective transformation of NO_2

17 to NO. In addition ozone, O_3, was measured by a UV-absorption photometer above canopy.

18 The photolysis rates of NO_2 and O_3, $J(NO_2)$ and $J(O^1D)$, respectively, were measured using

19 filter radiometers (Meteorologie consult, Königstein, Germany; Bohn et al., 2008). Two

20 $J(NO_2)$ sensors were positioned at 2 m and 24 m above ground, and one $J(O^1D)$ sensor was

21 placed at 24 m. Each measured the downwelling radiation. J(HONO) was calculated from

22 measured $J(NO_2)$ according to Trebs et al. (2009).

23 Relative humidity, temperature, wind direction, wind speed and other meteorological

24 parameters were monitored routinely by the SMEAR II station (Junninen et al., 2009;

25 http://www.atm.helsinki.fi/smartSMEAR/).

26 Evaluation of the boundary layer height was determined by radiosondes, measuring relative

27 humidity, temperature, pressure and altitude. From this data vertical profiles of the potential

28 temperature and the specific humidity were gained and hence the height and type of boundary

29 layer have been inferred (Ouwersloot et al., 2012).

A sample from the O-horizon of soil was taken at 10 June 2012 at the measurement site and was measured under controlled conditions in the lab according to Oswald et al. (2013) to investigate NO and HONO emission fluxes from soil.

3   Results

Some instruments were not running continuously during the measurement period of HUMMPA-COPEC 2010 from 12 July to 12 August 2010.. Besides specific instrument malfunctions, several power disruptions caused by thunderstorms often interrupted the measurement. From 17 July until 5 August, the two LOPAP instruments were running about 30 % of the time simultaneously. The dataset of other measurements is close to complete for this period, except for the OH measurement above the canopy and the $J(NO_2)$ measurement below the canopy (see Fig. 1).

Besides a linear relationship found between OH measured at the forest floor and above canopy (Fig. 2), the exponential relationship of $J(NO_2)$ at 2 m above ground and $J(NO_2)$ at 24 m above ground was used to interpolate OH above the canopy and $J(NO_2)$ below the canopy to extend the data base for PSS calculations.

3.1   Diel variation of HONO

In the clean environment of Hyytiälä diurnal variations of HONO were observed with mean daytime concentrations of 6.6 x 10^8 molecules cm^{-3} (27 ppt) at 1 m height and 6.5 x 10^8 molecules cm^{-3} (26 ppt) at 24 m height and mean nighttime concentrations of 9.1 x 10^8 molecules cm^{-3} (37 ppt) at 1 m height and 9.2 x 10^8 molecules cm^{-3} (37 ppt) at 24 m. Maximum values reached 3.2 x 10^9 molecules cm^{-3} (132 ppt) at 1 m and 3.4 x 10^9 molecules cm^{-3} (138 ppt) at 24 m at 22:30 in the late evening of 2 August. The concentrations reached a minimum after a short and strong rain event in the morning of the 25 July with values below 2 ppt close to the detection limit. This emphasise that no uncorrected interferences occur in clean air , analogue to the observations of Sörgel et al. (2011a). The concentrations of HONO were calculated according to Eq. (5) by assuming a PSS, only valid for conditions with short photolytic lifetime of HONO. In agreement with Kleffmann et al. (2005) and Sörgel et al. (2011a) the box plots in Figure 3 obviously show that for both heights the calculated

concentrations are often more than one order of magnitude lower than the measured concentration of HONO. While the PSS calculation shows a peak in the morning (6:30) at 1 m height and around mid-morning (8:30) at 24 m height, the daytime measured HONO values peak at noon (11:30).

Sörgel et al. (2011a) stated that $[HONO]_{PSS}$ correlates best with measured [NO] and found neither a correlation to measured [OH] nor to measured J(HONO). The correlation between $[HONO]_{PSS}$ and [NO] was strong also in our data (Fig. 4). The reasonable correlation of $[HONO]_{PSS}$ to measured [NO] might serve as a proxy for $[HONO]_{PSS}$ in general, since the ratio seems to be quite constant.

$$\frac{[HONO]_{PSS}}{[NO]} = \frac{k_2[OH]}{J(HONO)+k_3[OH]} \cong 0.02 \tag{6}$$

J(HONO) at PSS shows values of about 2 orders of magnitude higher than k_2 or k_3 multiplied with the [OH]. Since OH formation is strongly linked to radiation (Rohrer and Berresheim, 2006), its concentration positively correlates with J(HONO). Therefore, NO drives the variability of the PSS.

3.2 HONO budget calculations

The two gas phase reactions (R2) and (R3) together with the photolysis fail to explain the observed HONO concentrations. The comparison of observed changes in HONO concentrations with calculated values considering further sources and sinks leads to a more complete understanding of HONO cycling.

$$\underbrace{\frac{\Delta[HONO]}{\Delta t}}_{observed} = \underbrace{Sources - Sinks}_{calculated\ budget} \tag{7}$$

If the calculated difference in sources and sinks equals the observed value, the budget would be closed. As mentioned before, normally this is not the case and an unknown source is missing, which can be calculated according to Su et al. (2008b) and Sörgel et al. (2011a) with the following equation:

$$P_{unknown} = \underbrace{\frac{\Delta[\text{HONO}]}{\Delta t}}_{observed} - \underbrace{k_2[\text{NO}][\text{OH}]}_{\text{R2: } P_{NO+OH}} - \underbrace{k_4^{dark}[\text{NO}_2]}_{\text{R4: } P_{het}} + \underbrace{J(\text{HONO})[\text{HONO}]}_{\text{R1: } L_{phot}}$$

$$+ \underbrace{k_3[\text{OH}][\text{HONO}]}_{\text{R3: } L_{HONO+OH}} + \underbrace{\frac{v_{dep}}{h_{BL}}[\text{HONO}]}_{\text{dry deposition: } L_{dep}} \quad \underbrace{\pm T_h \pm T_v}_{\substack{\text{horizontal and} \\ \text{vertical transport}}} \qquad (8)$$

1   The resulting $P_{unknown}$ shows, that for most of the day there is still a large source missing (Fig.

2   5), at least for the period from 6:00 in the morning to 20:00 in the evening where HONO

3   lifetimes are below 30 min. This source is dominated by the photolytic loss of HONO that

4   forms the major sink for HONO and which exceeds the considered sources by far. Due to

5   generally low NO_2 values (below 2 ppb) the contribution of the dark heterogeneous NO_2

6   conversion (P_{het}) is very low, except for the early morning (before 7:00).

7   Not only the known sources seem to be small compared with the photolytic loss rate, also the

8   other sinks are negligible. E.g. with a deposition velocity for HONO of 2 cm s^{-1} (Harrison et

9   al., 1996; Su et al., 2008a), a mean daytime HONO concentration of 6.6 x 10^8 molecules cm^{-3}

10   and a typical boundary layer height at midday of about 1000 m, the deposition rate is 1.3 x

11   10^3 molecules cm^{-3} s^{-1}, i.e. 1.9 ppt/h and thus 1 to 2 orders of magnitude less than the

12   photolytic loss. The very low contribution of the dry deposition to HONO loss has already

13   been reported for other measurement campaigns (Su et al., 2008b; Sörgel et al., 2011a).

14   Horizontal transport, T_h, can strongly influence budget calculations in urban regions (Lee et

15   al., 2013). However, Hyytiälä is surrounded by uniform Boreal forest with up to 95 % of the

16   area within 5 km radius being forested, mostly by Scots pine and Spruce trees (Williams et

17   al., 2011) representing a homogenous fetch. Furthermore, with an average J(HONO) of about

18   6.7 x 10^{-4} s^{-1}, corresponding to a HONO lifetime of about 25 min and an average horizontal

19   wind speed of 2 m s^{-1} (maximum 7 m s^{-1}), direct emissions of HONO will be transported

20   about 3 km (maximum 10 km) within one lifetime. As most of the surrounding is covered by

21   forest and the next city Tampere, being nearly 50 km away there are no significant emission

22   sources within the fetch, thus horizontal advection of direct emissions will have little

23   influence on the HONO concentration during day. Therefore, the measurement site of

24   SMEAR II, with its homogeneous fetch is well suited to analyse the behaviour of $P_{unknown}$,

25   because all processes disturbing the analysis such as horizontal transport and direct emissions

26   can be neglected.

1 The contribution of vertical transport, T_v, to surface loss of HONO was estimated to be about

2 50 to 60 % (Wong et al., 2013), thus being the dominant loss process for HONO close to the

3 ground. Vertical mixing acts as a sink close to the surface and as an additional, yet

4 unaccounted source term at elevated levels. Hence, depending on the concentration gradient

5 of HONO and the ratio of photolysis, vertical transport can lead to reciprocal changes in

6 $P_{unknown}$ above canopy and below canopy when using the budget approach. Assuming the

7 unknown source is solely a ground source, $P_{unknown}$ is represented by T_v at elevated levels

8 ($P_{unknown} = T_v$). Nevertheless, without direct measurements of fluxes or the use of a chemistry

9 transport model, it is difficult to quantify T_v and its contribution remains uncertain. Without

10 explicitly considering T_v the budget approach is only reasonable for well mixed conditions

11 ($T_v = 0$).

12

3.3 Tracing the missing source

3.3.1 Influence of $J(NO_2)$ on $P_{unknown}$

15 Reactions (R5) and (R6-8) comprise several mechanisms of HONO formation from photolytic

16 dissociation of ortho-nitrophenols or light induced conversion of NO_2 on different reductive

17 surfaces, which are thought to be possible major sources for HONO during daytime

18 (Stemmler et al., 2006). The wavelength range for the proposed reactions is mostly covered

19 and well described by $J(NO_2)$. Therefore, a source corresponding to these reactions should

20 correlate to $J(NO_2)$ and especially the light induced conversion of NO_2 should correlate even

21 better with $P_{unknown}$ scaled to the NO_2 concentration (Fig. 6) (Sörgel et al., 2011a).

22 Scaling $P_{unknown}$ with the concentration of NO_2 on the ground leads to higher scattering of data

23 points, which might be caused by the higher noise levels of NO_2 data on ground. On the

24 contrary, the correlation above canopy is improved with similar scaling (figure 6 panels b and

25 d). The data points most affected belong to a period of rather cold and very clean conditions

26 with low NO_2 concentration of 1.6 to 2.9 x 10^9 molecules cm^{-3} (65 - 118 ppt) at the 23 July

27 (Williams et al., 2011). Since scaling $P_{unknown}$ above the canopy with corresponding NO_2

28 concentration increases the correlation with $J(NO_2)$, leads to the assumptions that either NO_2

29 plays a direct role in HONO formation or that in general NO_2 is a tracer for reactive nitrogen

30 (other potential HONO precursors) in the atmosphere. The fact that the correlation between

31 $P_{unknown}$ and $J(NO_2)$ below the canopy descends by scaling $P_{unknown}$ with NO_2 concentrations

can be either due to data scattering as mentioned above, due to HONO deposition on the forest floor (Sörgel et al., 2014) or due to different pathways of HONO and NO_2 formation below canopy. NO_2 below canopy is formed by shifted PSS below canopy and additional NO soil emissions oxidized by O_3 (Rummel et al., 2002). Opposed, due to low OH and NO values below canopy, the shift in the $[HONO]_{PSS}$ by reduced radiation below canopy has minor influence on HONO values (Fig. 3).

Since measurements of ortho-nitrophenols were not available, it is not possible to rule out that photolytic conversion of these compounds is a possible pathway. . However, from Eq. 3 we estimate that the concentration of o-NPs has to exceed the concentration of HONO by a factor of about 70 in order to compensate the photolytic loss of HONO. Taking the average daytime mixing ratio of HONO above canopy, the resulting mixing ratio of o-NPs would be about 1.8 ppb. Based on earlier studies (Bejan et al., 2006; Kourtchev et al., 2013), the concentration in clean environment such as Hyytiälä should be much lower and, thus, insignificant for HONO formation.

Another possible HONO source that depends on $J(NO_2)$ is the photolytic activation of organic surface reactants (R6-8) to reduce NO_2 and form HONO (Stemmler et al., 2006). But as previously mentioned, due to the lack of in-situ measurements of all quantities, this contribution could not be calculated. Obviously, it is likely that humic acids or similar compounds occur in the highly organic surrounding of the Boreal Forest. A strong hint on such a source might be the merging effect on the correlation of the $P_{unknown}$ with $J(NO_2)$ by scaling with the concentration of NO_2 above the canopy.

As radical formation is driven by sunlight as well, the recently proposed reaction of the HO_2-water complex with NO_2 as a potential HONO source (Li et al., 2014) might be correlated to radiation as well. The contribution of this source was estimated using the measured HO_2 concentration, a water vapour mixing ratio of 1.5 % (Hens et al. 2014) and the equilibrium constant (Sander et al., 2011) to calculate the complex formation. All calculations were made using 298 K and 1013 hPa as standard conditions. Hence, about 20 % of the HO_2 is complexed to water. The related HONO formation was calculated by using the rate constant (298 K, 1013 hPa) of the reaction of HO_2 and NO_2 without water according to Atkinson et al. (2004) and a 20 % enhancement of the reaction rate due to water vapour for conditions in the lower atmosphere (Sander and Peterson, 1984). Assuming a 100 % yield of HONO formation from the reaction of the complexed HO_2 with NO_2, as postulated by Li et al. (2014), the

3.3.2 Indirect influence of J(NO_2) on $P_{unknown}$

Besides the activation or the photolytic reaction of molecules by J(NO_2), the radiation influences also other parameters. One of these is the temperature of soil. The temperature of soil surface changes stronger and faster than in deeper layers of soil and is driven by radiative heating and cooling. Nitrification and denitrification by microorganisms takes place at the uppermost layer of soil and produces reactive nitrogen gases (Conrad, 1996). The rate of reactive nitrogen formation depends on many parameters like soil water content (SWC), pH, nutrient availability and, important in this context, the temperature of soil (Skopp et al., 1990; Oswald et al., 2013). Therefore, radiation can accelerate the formation of HONO by soil.

Since we did not measure the potential emission of HONO by soil in the field, a soil sample was taken afterwards and measured in the laboratory under controlled conditions according to Oswald et al. (2013). Concentrations of nutrients were quite low with ammonium being (1.60 ± 0.56) mg kg^{-1} N-NH$_4^+$, while NO$_3^-$ and NO$_2^-$ were not measureable (below LOD, i.e. 2 mg kg^{-1} N-NO$_3^-$ and 0.07 mg kg^{-1} N-NO$_2^-$). This is in good agreement with Korhonen et al. (2013), who found that the measurement site of Hyytiälä provides nutrient poor soils with NH$_4^+$ as the dominant inorganic nitrogen compound in the extract of soil organic layer (0.31 kg ha^{-1} N-NH$_4^+$) and the first 30 cm of mineral soil, while NO$_3^-$ forms only 0.6 % of it. The soil pH was very low with a value of about 3.0. The measurement of the soil sample showed no significant emission fluxes of HONO being below the limit of detection (0.08 ng m^{-2} s^{-1} =

0.288 µg m^{-2} h^{-1}) and emission fluxes of NO scattering around the limit of detection (1 ng m^{-2} s^{-1} = 3.6 µg m^{-2} h^{-1}). This is in good agreement with Oswald et al. (2013) and Maljanen et al. (2013), who both found that acidic forest soils tend to low emission fluxes of HONO. Maljanen et al. (2013) measured a maximum HONO flux of about 2 µg m^{-2} h^{-1} in terms of N. This would equal a source-strength of 7.1 x 10^3 molecules cm^{-3} s^{-1} (1 ppt h^{-1}) considering a boundary layer height of 1000 m and hence is negligible. The laboratory measurements of soil samples represent potential HONO emission fluxes as HONO can simultaneously be taken up by soil (Donaldson et al., 2014) or deposited to soil and reemitted as proposed by VandenBoer et al. (2013). In addition to emissions from the soil surface, the evaporation of dew can release HONO (He et al., 2006) also enhancing HONO fluxes in the early morning , when temperatures increase.

3.3.3 HONO formation by nitric acid photolysis

Adsorbed HNO$_3$ on humid surfaces (R9) seems to be more rapidly photolyzed than HNO$_3$ in the gas phase or in aqueous solution (Zhou et al., 2003; Abida et al., 2012). Therefore, leaves and needles loaded with nitric acid could be a major source of HONO in clean environments (Zhou et al., 2011). This mechanism has also been postulated as significant for the Boreal forest by Raivonen et al. (2006) to explain light induced NO$_y$ (NO, NO$_2$, HONO, HNO$_3$, peroxy acyl nitrate) emissions. To estimate the strength of this source we used a constant surface loading of HNO$_3$ of (8.3 ± 3.1) x 10^{-5} mol m^{-2}, which is close to one monolayer coverage (Zhou et al., 2011). The site investigated by Zhou et al. (2011) (PROPHET) was located in a mixed forest (~ 45° N), whereas the SMEAR II station is located in a boreal forest (~ 62 ° N) with the main tree species being scots pine. Nevertheless, both sites are rural forested sites with low local pollution and low NO$_x$ concentrations (Kulmala et al., 2000; Carroll et al., 2001). Therefore, we assume that the values derived by Zhou and co-workers (Zhou et al., 2011; Zhou et al., 2003) constitute a reasonable estimate for the conditions at the SMEAR site. The gas phase photolysis frequency for HNO$_3$ was parameterized using J(NO$_2$) and J(O^{1}D) (Sander et al., 2011). By adsorbing to the surface the absorption cross-sections of HNO$_3$ increases (Zhu et al., 2010; Abida et al., 2012), which is typically considered by the use of an empirical enhancement factor for natural systems (Zhou et al., 2011; Li et al., 2012). According to the similar environment in the study of Zhou and co-workers, we used their enhancement factor of 43 for Figure 7 (Zhou et al., 2003; Zhou et al., 2011).

1 The photolysis rate of surface adsorbed HNO_3 needs to be more than 400 times enhanced

2 compared to the photolysis in gas phase to explain $P_{unknown}$ of HONO (Fig. 7), which is still

3 within the estimated range (e.g. Zhu et al., 2008; Zhu et al., 2010¸Baergen and Donaldson,

4 2013). Nevertheless, the enhancement factor given by Zhou et al. (2011) is the only reported

5 value on the HONO formation rate (instead of HNO_3 photolysis rate) with respect to HNO_3

6 photolysis on natural surfaces. The error of $P_{HNO3(ads)}$ was calculated by using the standard

7 error of the surface loading of HNO_3 (Zhou et al., 2011). $J(HNO_3)$ constitutes the only

8 variable of $P_{HNO3(ads)}$ and is closely correlated to $J(NO_2)$ and $J(O^1D)$. This leads to a similar

9 correlation of $P_{unknown}$ with $P_{HNO3(ads)}$, like seen before with $J(NO_2)$ (Fig. 6). An additional

10 correlation might derive from the mechanism of HNO_3 photolysis, which is not fully

11 understood by now. Zhou et al. (2011) proposed that formed NO_2 during HNO_3 photolysis

12 reacts further with organics on the surface to form HONO (R6) as proposed by Stemmler et

13 al. (2006).

14

15 ## 3.4 Direct comparison of $P_{unknown}$ determined for two different heights

16 The ratio of $J(NO_2)$ at 24 m to $J(NO_2)$ at 2 m tracks the ratio of direct and diffuse radiation

17 penetrating the canopy. In the early morning the ratio increases, due to increasing direct

18 sunlight at the upper height. With the rising sun more direct sunlight penetrates the canopy

19 and a rather constant ratio develops which seems to be influenced by light patches. The ratio

20 of $P_{unknown}$ at 24 m to $P_{unknown}$ at 1 m during daytime is mainly above 1, except for the first

21 value where $P_{unknown}$ at both heights were still negative (Fig. 5). It strongly decreases from

22 values above 4 in the morning hours before it gets more stable with values around 2, but still

23 decreases until 2 hours after reaching the minimum of solar zenith angle (~43°). This diel

24 pattern can be explained by a combination of two processes; the change of the photolysis

25 frequency and the change of the concentration gradient (Fig. 8 a). The product of both, the

26 concentration and the photolysis frequency equals the photolytic loss rate, L_{phot}, which is the

27 unbalanced sink that determines $P_{unknown}$ (see Fig.5, Fig. 8 panels b and c). This is at least

28 valid from 8:30 to 17:30 where the contribution of other source and sink terms is less than 20

29 %. The HONO concentrations above the canopy are higher than below the canopy in the

30 morning (values over unity in Fig 8a). The gradients vary around zero from late morning to

31 noon and in the afternoon the concentrations below the canopy are higher. This closely

32 resembles the pattern found by Sörgel et al. (2011b) for a different forest ecosystem and

1 might therefore be typical for forests in general. Sörgel et al. (2011b) showed that this could

2 be attributed to different sources and sinks and the extent of the vertical exchange between the

3 forest and the atmosphere above. However, the variability of the ratios is smallest at minimum

4 solar zenith angle, which is the maximum of J(HONO). In a strict sense this is the only period

5 where the budget could be used for the determination of $P_{unknown}$ as the assumptions like well

6 mixed conditions (i.e. no concentration gradients), stationarity due to low lifetime of HONO

7 and potentially establishment of a PSS are fulfilled. During this period it could be questioned

8 if a budget below canopy makes sense as the portion below canopy where J(HONO) and thus

9 L_{phot} is reduced is very small compared to the whole boundary layer and recombination of NO

10 and OH below canopy has been found to play a minor role (section 3.2).

11 Impressively, $P_{unknown}$ correlates much better with L_{phot} (Fig. 8 b and c) than with J(NO$_2$) or

12 with the ratio of J(NO$_2$) to concentration of NO$_2$ (Fig. 6). This correlation (Fig. 8 b and c) is

13 not disturbed by any environmental condition, like the different regimes of stressed and

14 normal Boreal and even more astonishing it is not disturbed by the wild fire pollution plumes

15 transported from Russia (Nölscher et al., 2012). The almost perfect correlation of $P_{unknown}$

16 with L_{phot} is caused by the low contribution to the budget of all other processes (sources and

17 sinks) considered so far. Even including the parameterized HNO$_3$ photolysis (Sec. 3.4.3)

18 would not change much as it is only around 10 % of $P_{unknown}$. Therefore, the unknown source

19 is a process that exactly balances HONO photolysis or the sink itself is erroneous.

20 Nevertheless, this unbalanced photolysis term ($P_{unknown}$) has been found by applying different

21 techniques for HONO detection such as LOPAP (e.g., Kleffmann et al., 2005; Sörgel et al.,

22 2011a), denuder (Acker et al., 2006), differential optical absorption spectroscopy (Alicke et

23 al., 2002; Wong et al., 2012) and recently by using chemical ionization mass spectroscopy

24 (VandenBoer et al., 2013). Consequently, the unknown HONO source is very unlikely to be

25 caused by an instruments artefact. Additionally, recent flux measurements reported strong

26 daytime upward fluxes of HONO (Zhou et al., 2011, Ren et al., 2011), thus confirming a

27 ground source of HONO.

28

4 Conclusion

30 Concentrations of HONO during daytime exceeded the expected values calculated by the PSS

31 on average by a factor of about 20 and, thus, lead to an imbalanced budget above and below

32 canopy. An additional yet unknown source is required to balance the budget. However,

photolysis of ortho-nitrophenols is likely of minor importance under the clean environment of the Boreal Forest. A laboratory measurement of a soil sample in a dynamic chamber shows that direct soil emissions of HONO are insignificant for the measurement site in the Boreal Forest, featuring low soil nutrient content and low soil pH. However, the photolytically active radiation has a major influence on the budget of HONO, since the missing source resembles the photolytic daytime loss of HONO. It was not possible to clearly identify the most important source term, but a tendency for a possible coupling of different processes is most likely. For instance, the photolytic dissociation of HNO_3 adsorbed on humid surfaces and the conversion of NO_2 on photolytically activated surfaces, like humic acids, might occur simultaneously. However, the almost perfect correlation of $P_{unknown}$ with L_{phot} is caused by the low contribution of the considered processes to the budget and, hence, the unknown source is a process that exactly balances HONO photolysis. Further field investigations are needed to understand daytime HONO chemistry and its implication for the budget. Especially the role of vertical mixing needs to be analysed in more detail.

References

Abida, O., Du, J., and Zhu, L.: Investigation of the photolysis of the surface-adsorbed HNO_3 by combining laser photolysis with Brewster angle cavity ring-down spectroscopy, Chem. Phys. Lett., 534, 77-82, 10.1016/j.cplett.2012.03.034, 2012.

Acker, K., Moller, D., Wieprecht, W., Meixner, F. X., Bohn, B., Gilge, S., Plass-Dülmer, C., and Berresheim, H.: Strong daytime production of OH from HNO_2 at a rural mountain site, Geophysical Research Letters, 33, L02809, doi:02810.01029/02005GL024643, 2006.

Alicke, B., Platt, U., and Stutz, J.: Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, J. Geophys. Res., 107, LOP9-1-LOP9-LOP9-17, 10.1029/2000jd000075, 2002.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species, Atmospheric Chemistry and Physics, 4, 1461-1738, 2004.

Aubin, D. G., and Abbatt, J. P. D.: Interaction of NO_2 with hydrocarbon soot: Focus on HONO yield, surface modification, and mechanism, Journal of Physical Chemistry A, 111, 6263-6273, 2007.

Baergen, A. M., and Donaldson, D. J.: Photochemical Renoxification of Nitric Acid on Real Urban Grime, Environmental Science & Technology, 47, 815-820, 10.1021/es3037862, 2013.

Bejan, I., Abd El Aal, Y., Barnes, I., Benter, T., Bohn, B., Wiesen, P., and Kleffmann, J.: The photolysis of ortho-nitrophenols: a new gas phase source of HONO, Physical Chemistry Chemical Physics, 8, 2028-2035, 2006.

Bohn, B., Corlett, G. K., Gillmann, M., Sanghavi, S., Stange, G., Tensing, E., Vrekoussis, M., Bloss, W. J., Clapp, L. J., Kortner, M., Dorn, H. P., Monks, P. S., Platt, U., Plass-Dülmer, C., Mihalopoulos, N., Heard, D. E., Clemitshaw, K. C., Meixner, F. X., Prevot, A. S. H., and Schmitt, R.: Photolysis frequency measurement techniques: results of a comparison within the ACCENT project, Atmospheric Chemistry and Physics, 8, 5373-5391, 2008.

Carroll, M. A., Bertman, S. B., and Shepson, P. B.: Overview of the Program for Research on Oxidants: PHotochemistry, Emissions, and Transport (PROPHET) summer 1998 measurements intensive, J. Geophys. Res., 106, 24 275–24 288, 2001.

Conrad, R.: Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO), Microbiological Reviews, 60, 609-+, 1996.

De Jesus Medeiros, D., and Pimentel, A. S.: New insights in the atmospheric HONO formation: New pathways for N_2O_4 isomerization and NO_2 dimerization in the presence of water, Journal of Physical Chemistry A, 115, 6357-6365, 2011.

Donaldson, M. A., Berke, A. E., and Raff, J. D.: Uptake of Gas Phase Nitrous Acid onto Boundary Layer Soil Surfaces, Environmental Science & Technology, 48, 375-383, 10.1021/es404156a, 2014.

Elshorbany, Y. F., Steil, B., Brühl, C., and Lelieveld, J.: Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model, Atmospheric Chemistry and Physics, 12, 9977-10000, 10.5194/acp-12-9977-2012, 2012.

Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D., and Ramazan, K. A.: The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor

19

atmospheres: An integrated mechanism, Physical Chemistry Chemical Physics, 5, 223-242, 10.1039/b208564j, 2003.

Goodman, A. L., Bernard, E. T., and Grassian, V. H.: Spectroscopic Study of Nitric Acid and Water Adsorption on Oxide Particles: Enhanced Nitric Acid Uptake Kinetics in the Presence of Adsorbed Water, The Journal of Physical Chemistry A, 105, 6443-6457, 10.1021/jp003722l, 2001.

Harrison, R. M., Peak, J. D., and Collins, G. M.: Tropospheric cycle of nitrous acid, Journal of Geophysical Research-Atmospheres, 101, 14429-14439, 1996.

He, Y., Zhou, X., Hou, J., Gao, H., and Bertman, S. B.: Importance of dew in controlling the air-surface exchange of HONO in rural forested environments, Geophysical Research Letters, 33, L02813, 10.1029/2005GL024348, 2006.

Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere, Environmental Science & Technology, 35, 3207-3212, 10.1021/es000303t, 2001.

Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A. C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of HO_x radicals in a boreal forest, Atmos. Chem. Phys. Discuss., 13, 28561-28629, 10.5194/acpd-13-28561-2013, 2013.

Hosaynali Beygi, Z., Fischer, H., Harder, H. D., Martinez, M., Sander, R., Williams, J., Brookes, D. M., Monks, P. S., and Lelieveld, J.: Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state, Atmos. Chem. Phys., 11, 8497-8513, 10.5194/acp-11-8497-2011, 2011.

Junninen, H., Lauri, A., Keronen, P., Aalto, P., Hiltunen, V., Hari, P., and Kulmala, M.: Smart-SMEAR: on-line data exploration and visualization tool for SMEAR stations., Boreal Environ. Res., 14, 447-457, 2009.

Kleffmann, J., Heland, J., Kurtenbach, R., Lörzer, J., and Wiesen, P.: A new instrument (LOPAP) for the detection of nitrous acid (HONO), Environmental Science and Pollution Research, 48-54, 2002.

Kleffmann, J., Kurtenbach, R., Lörzer, J., Wiesen, P., Kalthoff, N., Vogel, B., and Vogel, H.: Measured and simulated vertical profiles of nitrous acid - Part I: Field measurements, Atmospheric Environment, 37, 2949-2955, 10.1016/s1352-2310(03)00242-5, 2003.

Kleffmann, J., Gavriloaiei, T., Hofzumahaus, A., Holland, F., Koppmann, R., Rupp, L., Schlosser, E., Siese, M., and Wahner, A.: Daytime formation of nitrous acid: A major source of OH radicals in a forest, Geophysical Research Letters, 32, 2005.

Kleffmann, J.: Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer, ChemPhysChem, 8, 1137-1144, 2007.

Korhonen, J. F. J., Pihlatie, M., Pumpanen, J., Aaltonen, H., Hari, P., Levula, J., Kieloaho, A. J., Nikinmaa, E., Vesala, T., and Ilvesniemi, H.: Nitrogen balance of a boreal Scots pine forest, Biogeosciences, 10, 1083-1095, 10.5194/bg-10-1083-2013, 2013.

Kourtchev, I., Fuller, S., Aalto, J., Ruuskanen, T. M., McLeod, M. W., Maenhaut, W., Jones, R., Kulmala, M., and Kalberer, M.: Molecular Composition of Boreal Forest Aerosol from Hyytiala, Finland, Using Ultrahigh Resolution Mass Spectrometry, Environmental Science & Technology, 47, 4069-4079, 10.1021/es3051636, 2013.

Kraus, A., and Hofzumahaus, A.: Field measurements of atmospheric photolysis frequencies for O_3, NO_2, HCHO, CH_3CHO, H_2O_2, and HONO by UV spectroradiometry, J. Atmos. Chem., 31, 161-180, 1998.

Kubota, M., and Asami, T.: Volatilization of nitrous-acid from upland soils, Soil Sci. Plant Nutr., 31, 27-34, 1985.

Kulmala, M., Rannik, U., Pirjola, L., Dal Maso, M., Karimäki, J., Asmi, A., Jäppinen, A., Karhu, V., Korhonen, H., Malvikko, S. P., Puustinen, A., Raittila, J., Romakkaniemi, S., Suni, T., Yli-Koivisto, S., Paatero, J., Hari, P. and Vesala, T.: Characterization of atmospheric trace gas and aerosol concentrations at forest sites in southern and northern Finland using back trajectories, Boreal Environ. Res., 5, 315–336, 2000.

Lammel, G., and Cape, J. N.: Nitrous acid and nitrite in the atmosphere, Chemical Society Reviews, 25, 361-369, 1996.

Lee, B. H., Wood, E. C., Herndon, S. C., Lefer, B. L., Luke, W. T., Brune, W. H., Nelson, D. D., Zahniser, M. S., and Munger, J. W.: Urban measurements of atmospheric nitrous acid: A caveat on the interpretation of the HONO photostationary state, Journal of Geophysical Research: Atmospheres, 118, 2013JD020341, 10.1002/2013JD020341, 2013.

Li, X., Brauers, T., Haseler, R., Bohn, B., Fuchs, H., Hofzumahaus, A., Holland, F., Lou, S., Lu, K. D., Rohrer, F., Hu, M., Zeng, L. M., Zhang, Y. H., Garland, R. M., Su, H., Nowak, A., Wiedensohler, A., Takegawa, N., Shao, M., and Wahner, A.: Exploring the atmospheric chemistry of nitrous acid (HONO) at a rural site in Southern China, Atmospheric Chemistry and Physics, 12, 1497-1513, 10.5194/acp-12-1497-2012, 2012.

Maljanen, M., Yli-Pirilä, P., Hytönen, J., Joutsensaari, J., and Martikainen, P. J.: Acidic northern soils as sources of atmospheric nitrous acid (HONO), Soil Biology and Biochemistry, 67, 94-97, http://dx.doi.org/10.1016/j.soilbio.2013.08.013, 2013.

Monge, M. E., D'Anna, B., Mazri, L., Giroir-Fendler, A., Ammann, M., Donaldson, D. J., and George, C.: Light changes the atmospheric reactivity of soot, Proc. Natl. Acad. Sci. U. S. A., 107, 6605-6609, 10.1073/pnas.0908341107, 2010.

Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., de Arellano, J. V. G., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, Atmospheric Chemistry and Physics, 12, 8257-8270, 10.5194/acp-12-8257-2012, 2012.

Novelli, A., Hens, K., Tatum Ernest, C., Kubistin, D., Regelin, E., Elste, T., Plass-Dülmer, C., Martinez, M., Lelieveld, J., and Harder, H.: Characterisation of an inlet pre-injector laser induced fluorescence instrument for the measurement of ambient hydroxyl radicals, Atmos. Meas. Tech. Discuss., 7, 819-858, 10.5194/amtd-7-819-2014, 2014.

Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Röser, A., Sorgel, M., Pöschl, U., Hoffmann, T., Andreae, M. O., Meixner, F. X., and Trebs, I.: HONO Emissions from Soil Bacteria as a Major Source of Atmospheric Reactive Nitrogen, Science, 341, 1233-1235, 10.1126/science.1242266, 2013.

Ouwersloot, H. G., de Arellano, J. V. G., Nölscher, A. C., Krol, M. C., Ganzeveld, L. N., Breitenberger, C., Mammarella, I., Williams, J., and Lelieveld, J.: Characterization of a boreal convective boundary layer and its impact on atmospheric chemistry during HUMPPA-COPEC-2010, Atmospheric Chemistry and Physics, 12, 9335-9353, 10.5194/acp-12-9335-2012, 2012.

Park, J. Y., and Lee, Y. N.: Solubility and decomposition kinetics of nitrous-acid in aqueous-solution, J. Phys. Chem., 92, 6294-6302, 10.1021/j100333a025, 1988.

Perner, D., and Platt, U.: Detection of nitrous-acid in the atmosphere by differential optical-absorption, Geophysical Research Letters, 6, 917-920, 10.1029/GL006i012p00917, 1979.

Petäjä, T., Mauldin Iii, R. L., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T., and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9, 7435-7448, 10.5194/acp-9-7435-2009, 2009.

Raivonen, M., Bonn, B., Sanz, M. J., Vesala, T., Kulmala, M., and Hari, P.: UV-induced NOy emissions from Scots pine: Could they originate from photolysis of deposited HNO3?, Atmospheric Environment, 40, 6201-6213, 10.1016/j.atmosenv.2006.03.063, 2006.

Ramazan, K. A., Syomin, D., and Finlayson-Pitts, B. J.: The photochemical production of HONO during the heterogeneous hydrolysis of NO_2, Physical Chemistry Chemical Physics, 6, 3836-3843, 2004.

Ren, X., Sanders, J. E., Rajendran, A., Weber, R. J., Goldstein, A. H., Pusede, S. E., Browne, E. C., Min, K. E., and Cohen, R. C.: A relaxed eddy accumulation system for measuring vertical fluxes of nitrous acid, Atmospheric Measurement Techniques, 4, 2093-2103, 10.5194/amt-4-2093-2011, 2011.

Rohrer, F., and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184-187, 10.1038/nature04924, 2006.

Rummel, U., Ammann, C., Gut, A., Meixner, F. X., and Andreae, M. O.: Eddy covariance measurements of nitric oxide flux within an Amazonian rain forest, J. Geophys. Res., 107, LBA17-11-19, 10.1029/2601jd000520, 2002.

Sander, S. P., Abbatt, J. P. D., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, in: JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011.

Sander, S. P. and Peterson, M.: Kinetics of the reaction $HO_2 + NO_2 + M => H0_2N0_2 + M$, J. Phys. Chem., 88, 1566-1571, 1984.

Skopp, J., Jawson, M. D., and Doran, J. W.: Steady-state aerobic microbial activity as a function of soil-water content, Soil Science Society of America Journal, 54, 1619-1625, 1990.

Sörgel, M., Regelin, E., Bozem, H., Diesch, J. M., Drewnick, F., Fischer, H., Harder, H., Held, A., Hosaynali-Beygi, Z., Martinez, M., and Zetzsch, C.: Quantification of the unknown HONO daytime source and its relation to NO_2, Atmospheric Chemistry and Physics, 11, 10433-10447, 10.5194/acp-11-10433-2011, 2011a.

Sörgel, M., Trebs, I., Serafimovich, A., Moravek, A., Held, A., and Zetzsch, C.: Simultaneous HONO measurements in and above a forest canopy: influence of turbulent exchange on mixing ratio differences, Atmospheric Chemistry and Physics, 11, 841-855, 10.5194/acp-11-841-2011, 2011b.

Sörgel, M., Wu, D., Trebs, I., and Held, A.: A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment., submitted to Atmos. Chem. Phys. Discuss., 2014.

Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195-198, 2006.

Stemmler, K., Ndour, M., Elshorbany, Y., Kleffmann, J., D'Anna, B., George, C., Bohn, B., and Ammann, M.: Light induced conversion of nitrogen dioxide into nitrous acid on

submicron humic acid aerosol, Atmospheric Chemistry and Physics, 7, 4237-4248, 2007.

Su, H., Cheng, Y. F., Cheng, P., Zhang, Y. H., Dong, S., Zeng, L. M., Wang, X., Slanina, J., Shao, M., and Wiedensohler, A.: Observation of nighttime nitrous acid (HONO) formation at a non-urban site during PRIDE-PRD2004 in China, Atmospheric Environment, 42, 6219-6232, 10.1016/j.atmosenv.2008.04.006, 2008a.

Su, H., Cheng, Y. F., Shao, M., Gao, D. F., Yu, Z. Y., Zeng, L. M., Slanina, J., Zhang, Y. H., and Wiedensohler, A.: Nitrous acid (HONO) and its daytime sources at a rural site during the 2004 PRIDE-PRD experiment in China, Journal of Geophysical Research-Atmospheres, 113, 10.1029/2007jd009060, 2008b.

Su, H., Cheng, Y., Oswald, R., Behrendt, T., Trebs, I., Meixner, F. X., Andreae, M. O., Cheng, P., Zhang, Y., and Pöschl, U.: Soil Nitrite as a Source of Atmospheric HONO and OH Radicals, Science, 333, 1616-1618, 10.1126/science.1207687, 2011.

Trebs, I., Bohn, B., Ammann, C., Rummel, U., Blumthaler, M., Königstedt, R., Meixner, F. X., Fan, S., and Andreae, M. O.: Relationship between the NO_2 photolysis frequency and the solar global irradiance, Atmospheric Measurement Techniques, 2, 725-739, 2009.

Twigg, M. M., House, E., Thomas, R., Whitehead, J., Phillips, G. J., Famulari, D., Fowler, D., Gallagher, M. W., Cape, J. N., Sutton, M. A., and Nemitz, E.: Surface/atmosphere exchange and chemical interactions of reactive nitrogen compounds above a manured grassland, Agricultural and Forest Meteorology, 151, 1488-1503, 10.1016/j.agrformet.2011.06.005, 2011.

==Tyndall, G. S., Orlando, J. J., and Calvert, J. G.: Upper limit for the rate coefficient for the reaction HO2+NO2 => HONO + O2, Environ. Sci. Technol., 29, 202–206, 1995.==

VandenBoer, T. C., Brown, S. S., Murphy, J. G., Keene, W. C., Young, C. J., Pszenny, A. A. P., Kim, S., Warneke, C., de Gouw, J. A., Maben, J. R., Wagner, N. L., Riedel, T. P., Thornton, J. A., Wolfe, D. E., Dubé, W. P., Öztürk, F., Brock, C. A., Grossberg, N., Lefer, B., Lerner, B., Middlebrook, A. M., and Roberts, J. M.: Understanding the role of the ground surface in HONO vertical structure: High resolution vertical profiles during NACHTT-11, Journal of Geophysical Research: Atmospheres, 118, 10,155-110,171, 10.1002/jgrd.50721, 2013.

Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petaja, T., Rinne, J., Back, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nolscher, A., Johnson, A. M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M. J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P. J., Ebben, C. J., Geiger, F. M., Corrigan, A. L., Russell, L. M., Ouwersloot, H. G., de Arellano, J. V. G., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C. J., Bertelmann, M., Kollner, F., Hoffmann, T., Valverde, J., Gonzalez, D., Riekkola, M. L., Kulmala, M., and Lelieveld, J.: The summertime Boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences, Atmospheric Chemistry and Physics, 11, 10599-10618, 10.5194/acp-11-10599-2011, 2011.

Wong, K. W., Tsai, C., Lefer, B., Haman, C., Grossberg, N., Brune, W. H., Ren, X., Luke, W., and Stutz, J.: Daytime HONO vertical gradients during SHARP 2009 in Houston, TX, Atmospheric Chemistry and Physics, 12, 635-652, 10.5194/acp-12-635-2012, 2012.

Wong, K. W., Tsai, C., Lefer, B., Grossberg, N., and Stutz, J.: Modeling of daytime HONO vertical gradients during SHARP 2009, Atmos. Chem. Phys., 13, 3587-3601, 10.5194/acp-13-3587-2013, 2013.

Yabushita, A., Enami, S., Sakamoto, Y., Kawasaki, M., Hoffmann, M. R., and Colussi, A. J.: Anion-Catalyzed Dissolution of NO_2 on Aqueous Microdroplets, The Journal of Physical Chemistry A, 113, 4844-4848, 10.1021/jp900685f, 2009.

York, D., Evensen, N. M., Martínez, M. L., and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, American Journal of Physics, 72, 367-375, doi:http://dx.doi.org/10.1119/1.1632486, 2004.

Zhang, N., Zhou, X., Bertman, S., Tang, D., Alaghmand, M., Shepson, P. B., and Carroll, M. A.: Measurements of ambient HONO concentrations and vertical HONO flux above a northern Michigan forest canopy, Atmospheric Chemistry and Physics, 12, 8285-8296, 10.5194/acp-12-8285-2012, 2012.

Zhou, X. L., Gao, H. L., He, Y., Huang, G., Bertman, S. B., Civerolo, K., and Schwab, J.: Nitric acid photolysis on surfaces in low-NO_x environments: Significant atmospheric implications, Geophysical Research Letters, 30, 2217   10.1029/2003gl018620, 2003.

Zhou, X. L., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P. B., Carroll, M. A., Griffith, S., Dusanter, S., and Stevens, P. S.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nat. Geosci., 4, 440-443, 10.1038/ngeo1164, 2011.

Zhu, C., Xiang, B., Zhu, L., and Cole, R.: Determination of absorption cross sections of surface-adsorbed HNO_3 in the 290–330 nm region by Brewster angle cavity ring-down spectroscopy, Chem. Phys. Lett., 458, 373-377, http://dx.doi.org/10.1016/j.cplett.2008.04.125, 2008.

Zhu, C. Z., Xiang, B., Chu, L. T., and Zhu, L.: 308 nm Photolysis of Nitric Acid in the Gas Phase, on Aluminum Surfaces, and on Ice Films, Journal of Physical Chemistry A, 114, 2561-2568, 10.1021/jp909867a, 2010.

1
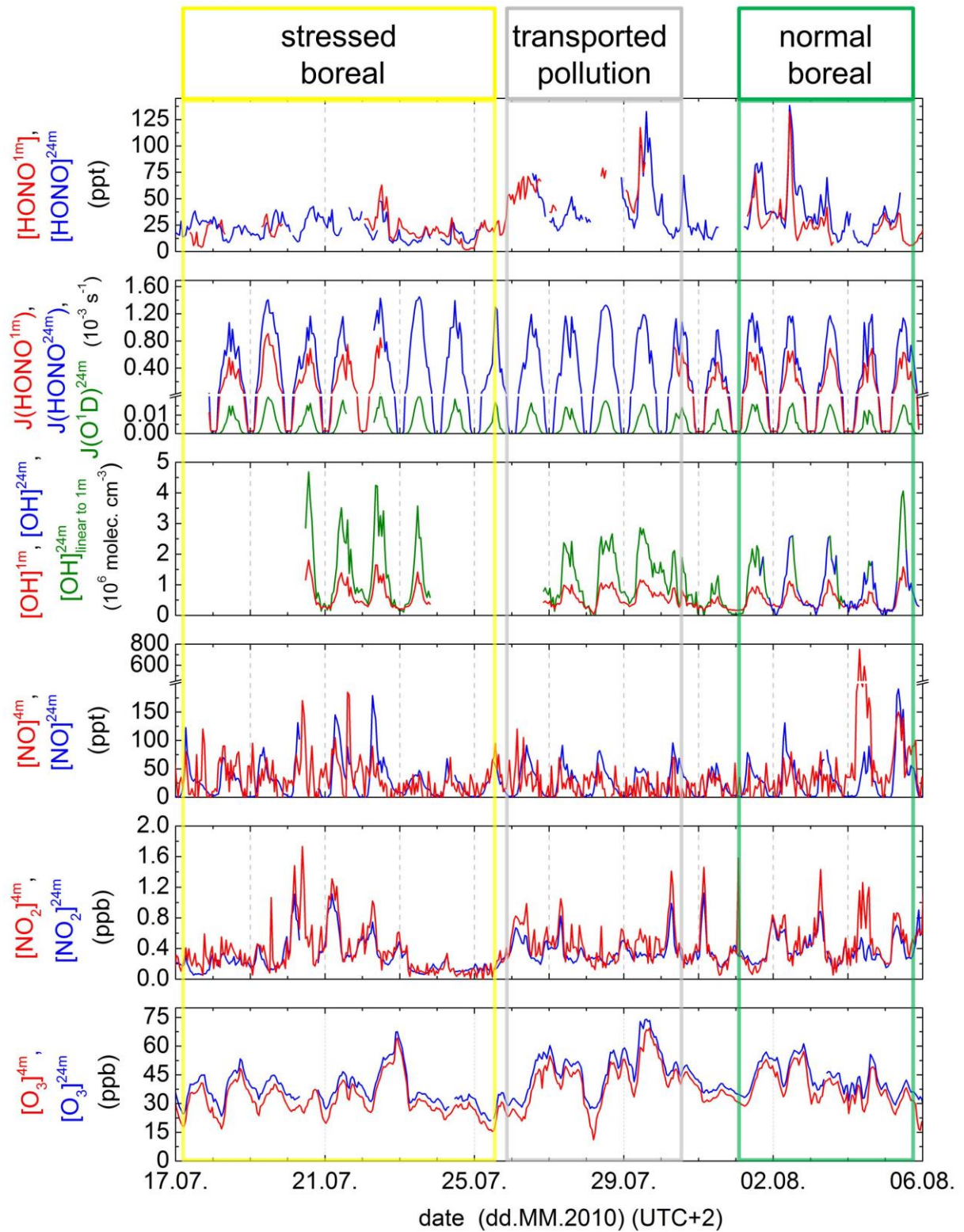2 Figure 1. Overview of the measured concentration of different trace gases and the photolysis
3 frequencies J(HONO) and J(O¹D). The linearly connected data points represent 60 min
4 average values. Mixing ratios or concentrations are shown for the period where HONO was
5 measured at both heights. $[OH]_{linear\ to\ 1m}^{24m}$ was used to fill the gaps in OH measurements above

25

1 the canopy (see Fig. 2 a). <mark>Coloured boxes mark the respective regimes of "normal boreal"</mark>

2 <mark>(green), "stressed boreal" (yellow) and "transported pollution" (grey).</mark>

3
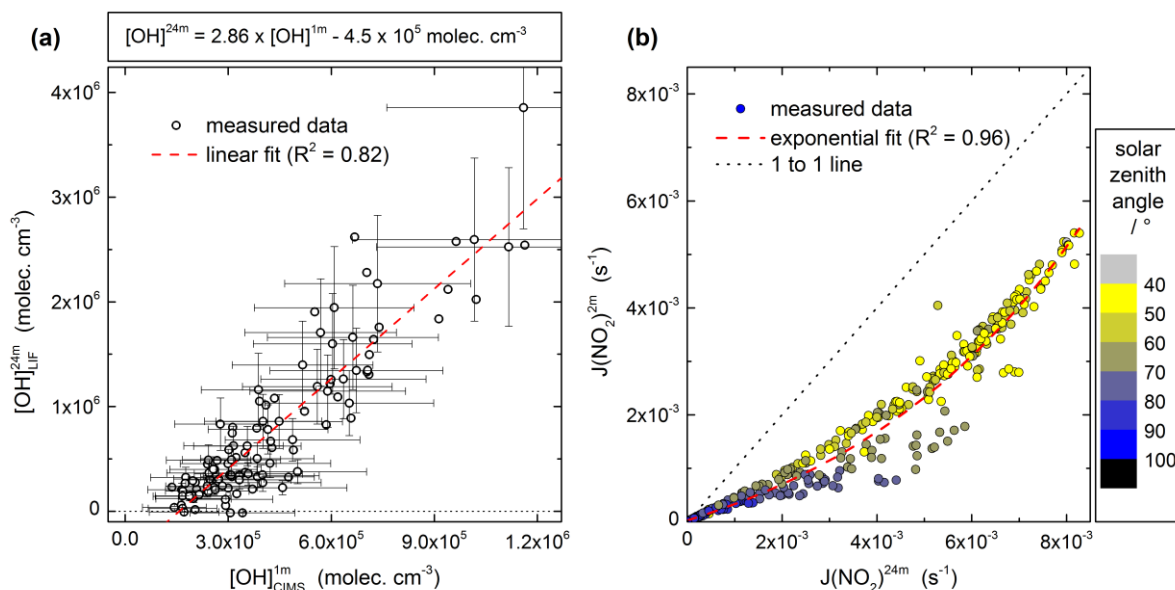
4
5 Figure 2. (A) The linear correlation of OH concentration below and above the canopy was

6 used for interpolating data of OH concentration above the canopy. (B) Similar to (A) the

7 exponential correlation of measured photolysis frequency below and above the canopy was

8 used to interpolate data of $J(NO_2)$ below the canopy. Color code of dots represents the solar

9 zenith angle. Additionally the 1 to 1 line is shown as dashed line.

10
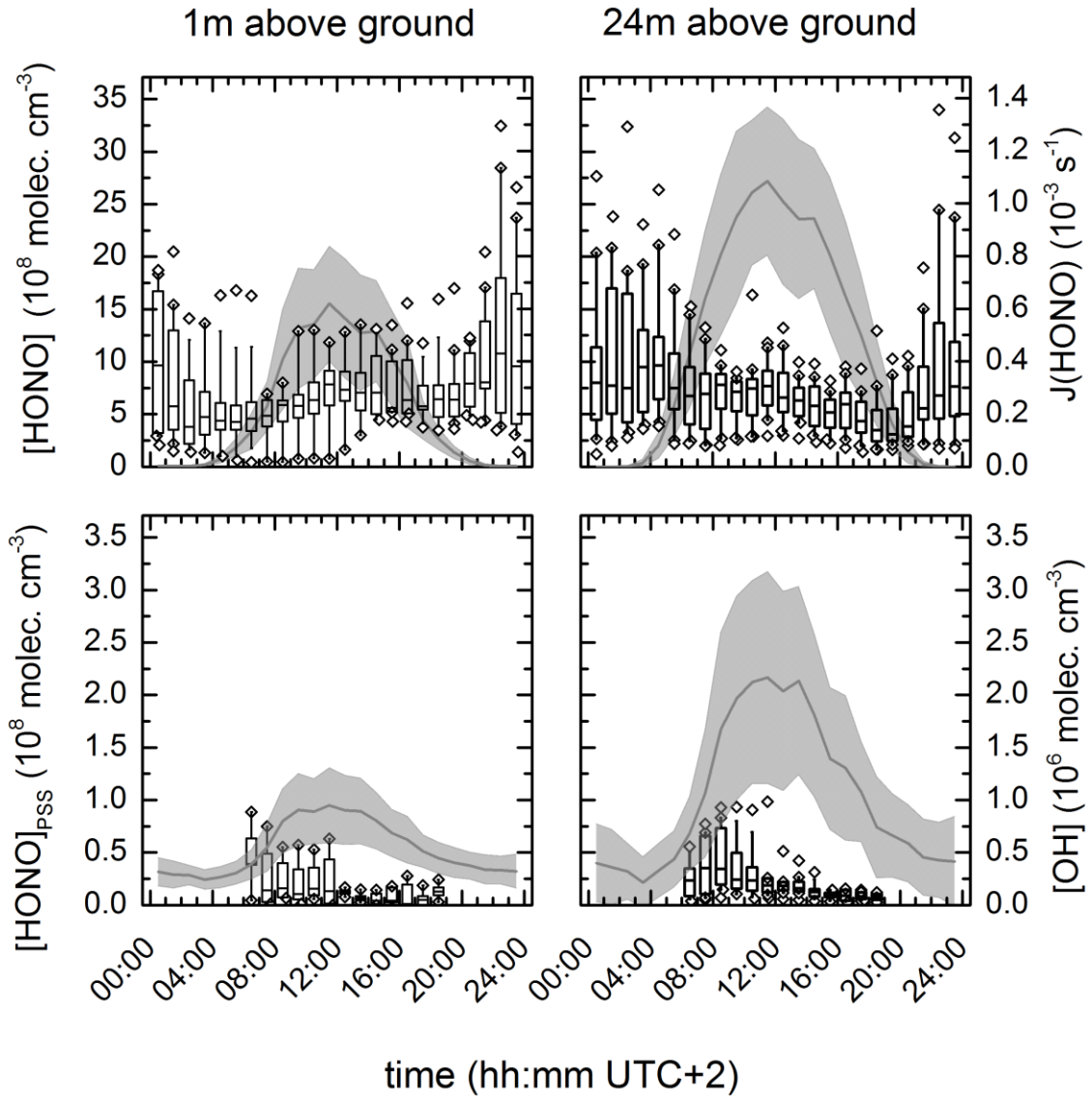
1
2 Figure 3. Upper panels show box plots of the diel cycle of HONO measured at 1 m and 24 m,
3 respectively and the average corresponding J(HONO) with standard deviation (grey shaded
4 line). Lower panels show box plots for the calculated PSS concentration of HONO for the
5 heights of 1 m and 24 m, respectively, during daytime (lifetime of HONO below 4 h) where
6 PSS is possibly attained. Additionally, the average concentration of OH with standard
7 deviation (grey shaded line) for the two respective heights is presented. The boxes represent
8 the 25 to 75 percentile, the line within the box is the median, the bars show the 10 to 90
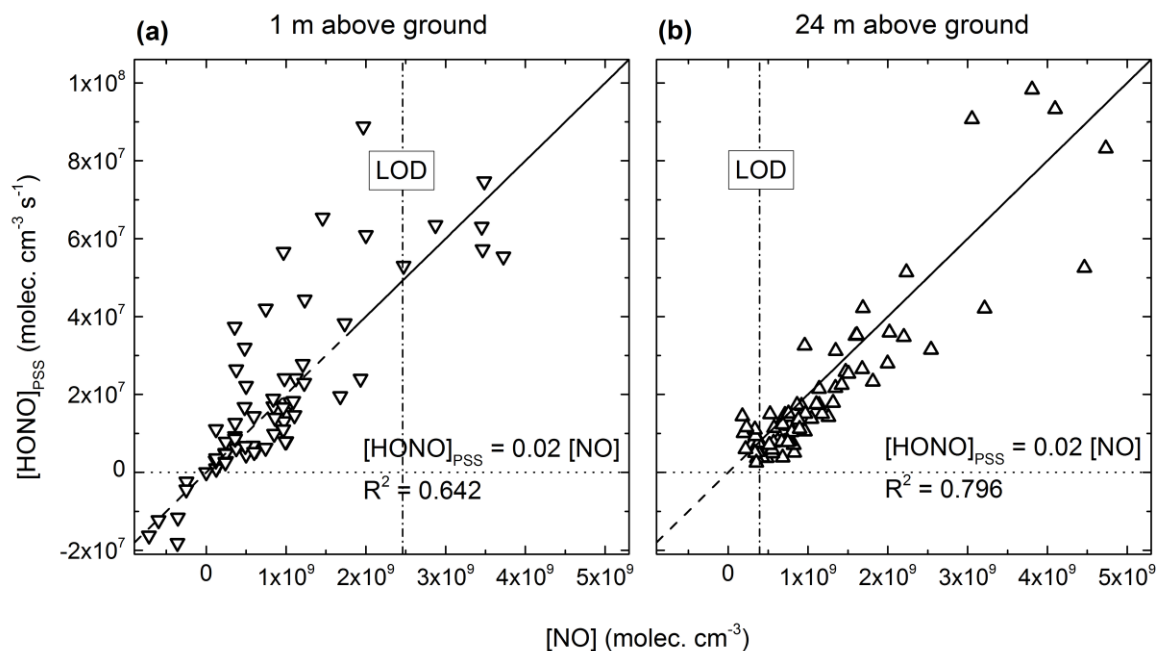9 percentile and outliers are marked as open diamonds.

10

Figure 4. The PSS concentration of HONO, $[HONO]_{PSS}$, at 1 m measurement height (a) and at 24 m measurement height (b) is plotted against the concentration of NO at the corresponding heights. The dashed-dotted vertical line reflects the lower limit of detection (LOD) for each NO measurement. The linear fit using a fixed slope of 0.02 and no offset leads to a reasonable correlations between $[HONO]_{PSS}$ and [NO] in both cases.
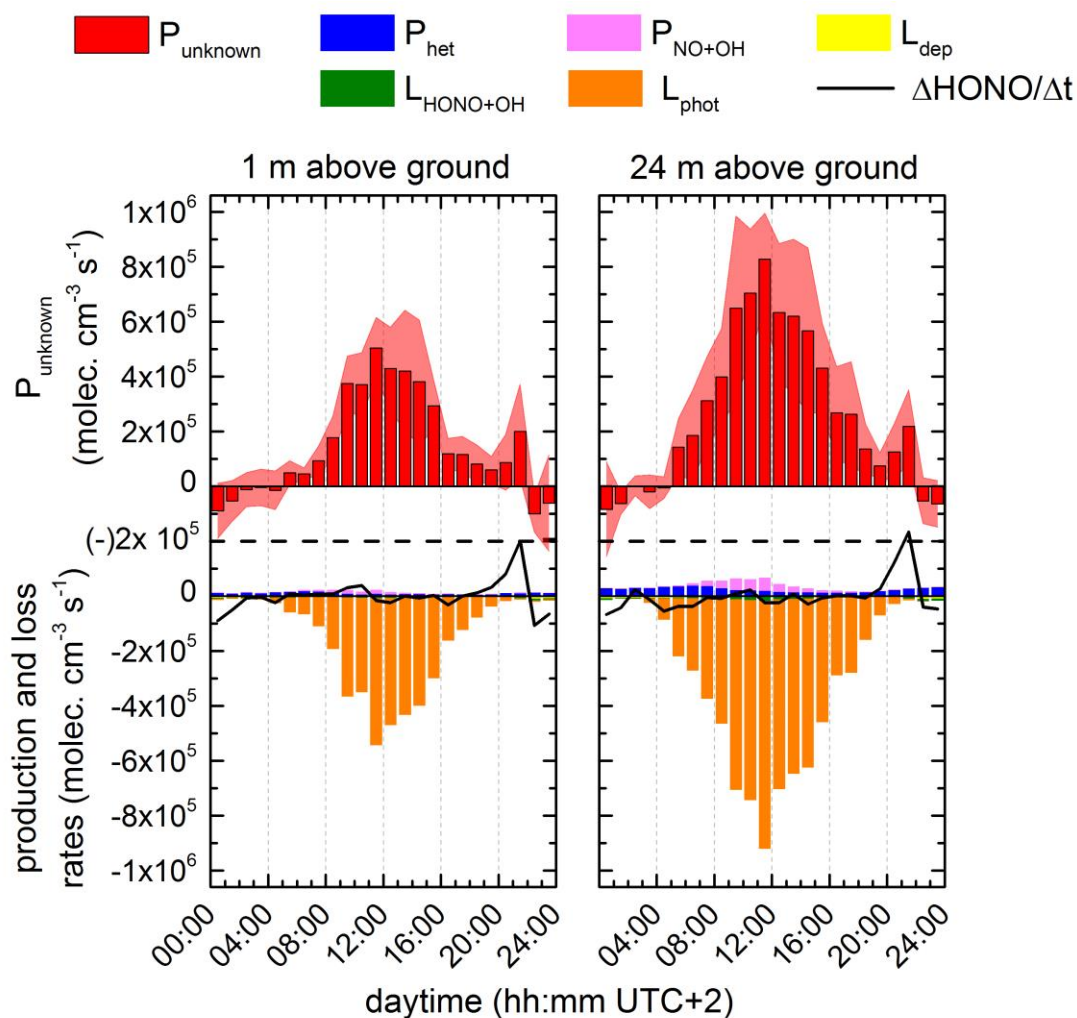
Figure 5. The diel variation of $P_{unknown}$ (red bars, upper panel) with standard deviation (red shade), the single production and loss terms (coloured bars, lower panel) and the change in HONO concentration ($\Delta HONO/\Delta t$) (black line, lower panel) for the two heights are shown. The scales and units at the left and right hand y-axis are valid for both measurement heights and were chosen for an easy comparison with other publications.
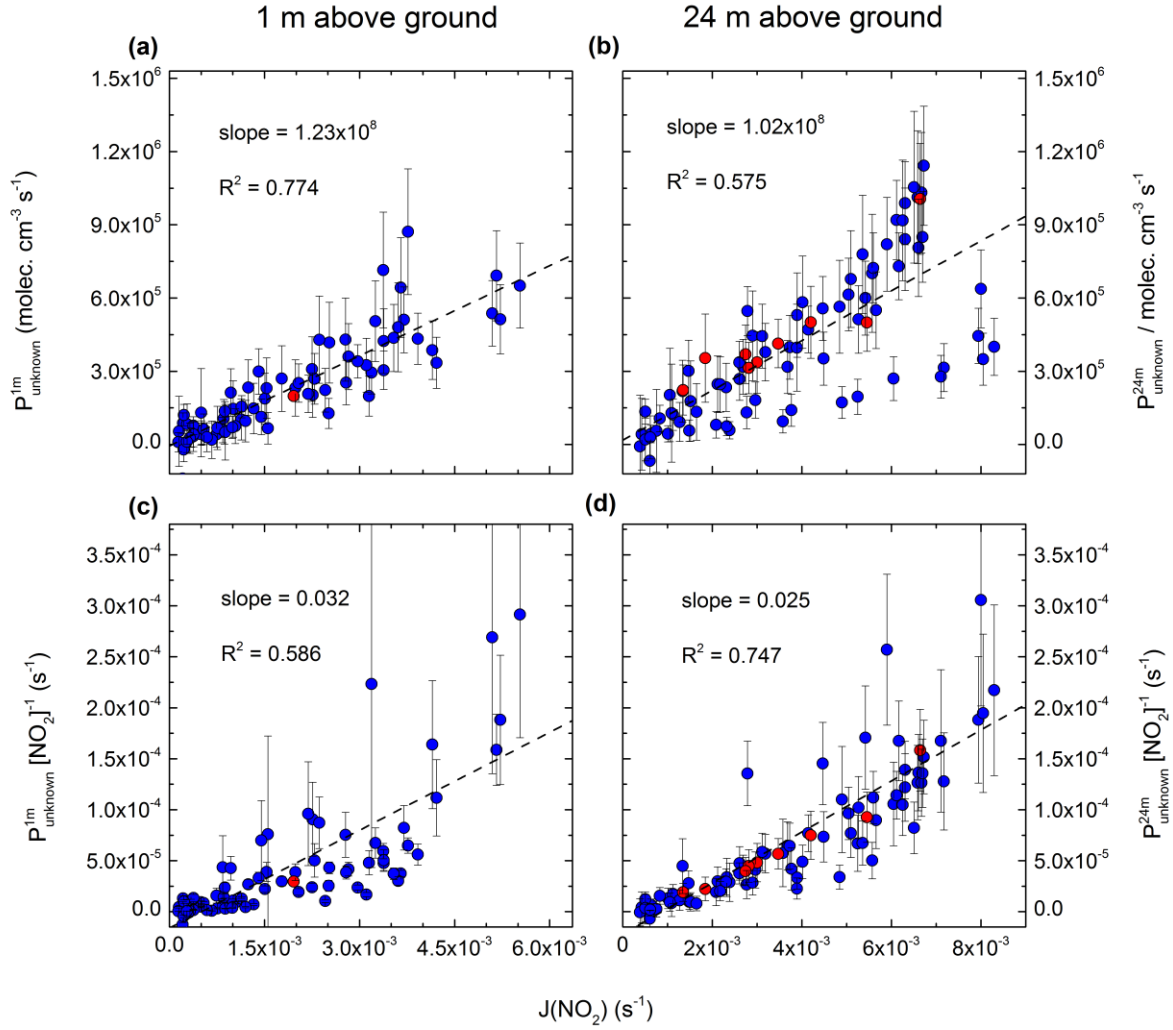
1 m above ground

(a)

slope = 1.23x10^8

R^2 = 0.774

24 m above ground

(b)

slope = 1.02x10^8

R^2 = 0.575

(c)

slope = 0.032

R^2 = 0.586

(d)

slope = 0.025

R^2 = 0.747

$J(NO_2)$ (s^{-1})

1
2 Figure 6. In the upper panels, (a) and (b), $P_{unknown}$ for both measurement heights is linearly
3 correlated with corresponding $J(NO_2)$. In the lower panels, (c) and (d), $P_{unknown}$ is scaled by
4 the NO_2 concentration and still linearly correlated with $J(NO_2)$. Blue dots denote budget data
5 availability at both heights, whereas red dots are available only at the respective measurement
6 height. Linear fits refer to total data available (blue and red),
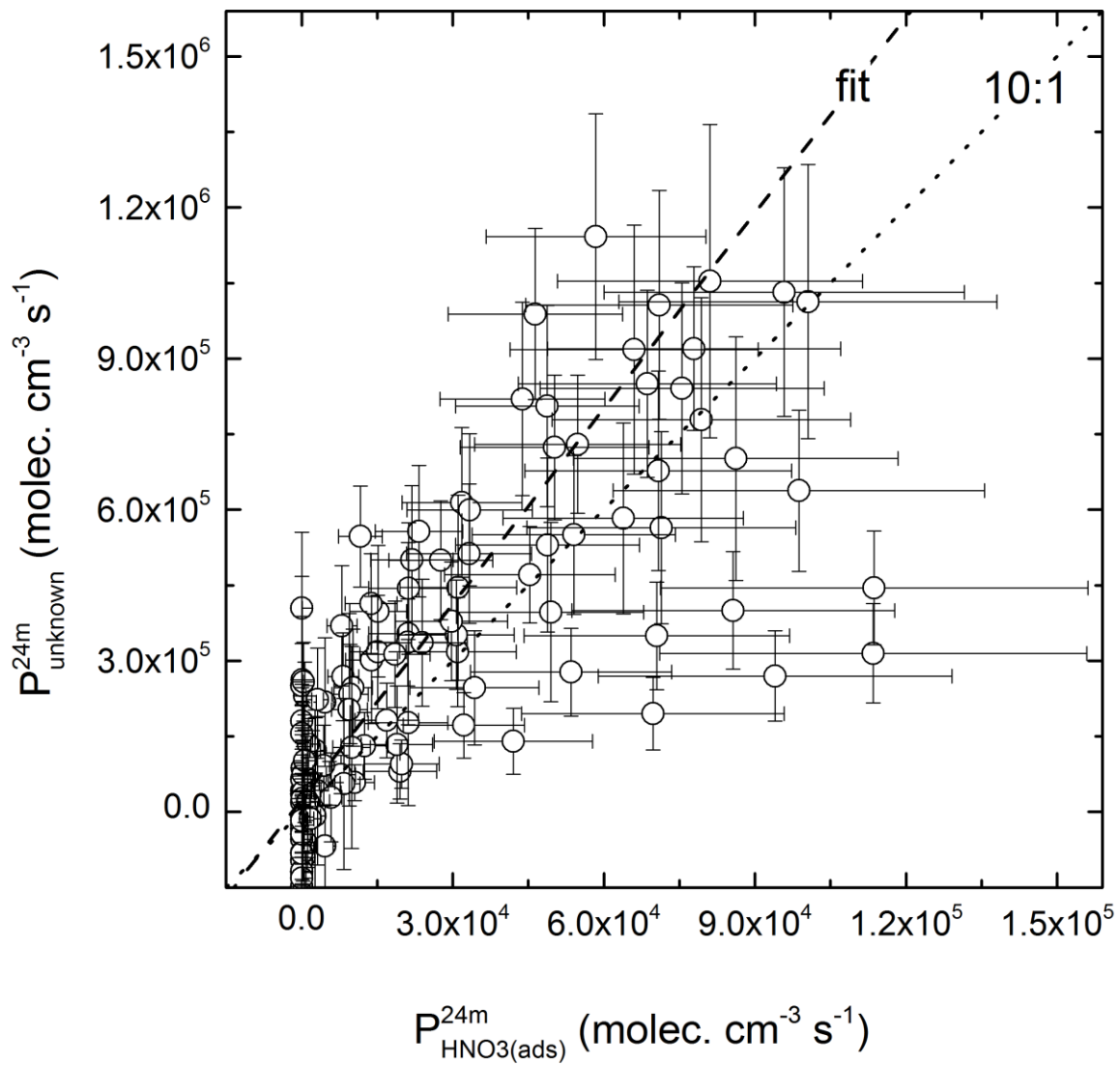
7

1
2 Figure 7. $P_{unknown}$ at the measurement height of 24 m during daytime is plotted against the
3 production of HONO from photolysis of adsorbed HNO_3 on leaf surfaces, $P_{HNO3(ads)}$. With an
4 enhancement factor of 43 and a surface loading of $(8.3 \pm 3.1) \times 10^{-5}$ mol m^{-2} it might explain
5 up to 10 % of $P_{unknown}$, indicated by the 10 to 1 line (dotted line). The York linear fit (York et
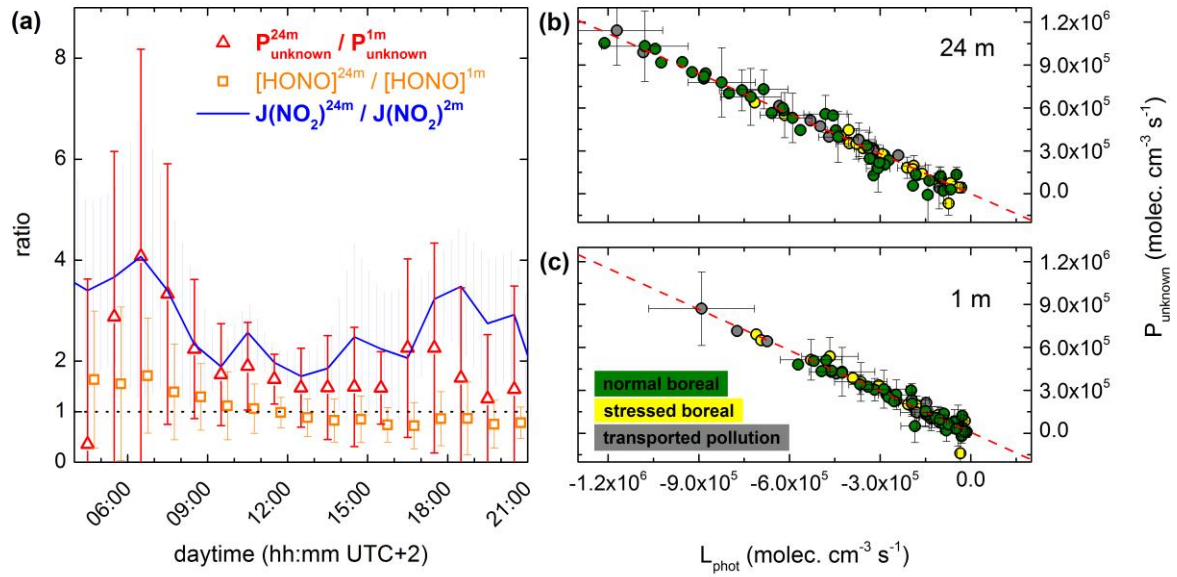6 al., 2004) yields in $P_{unknown} = (12.9 \pm 1.0) \times P_{HNO3(ads)} + (2.4 \pm 1.1) \times 10^4$ molecules cm^{-3} s^{-1}.

7

1
2 Figure 8. (a) The average ratio of $P_{unknown}^{24m}$ to $P_{unknown}^{1m}$ (red triangles), the average ratio of

3 $[HONO]^{24m}$ to $[HONO]^{1m}$ (orange squares) and the average ratio of $J(NO_2)^{24m}$ to $J(NO_2)^{2m}$

4 (blue line) change during daytime (lifetime of HONO < 4 h). For clarity a second x-

5 coordinate for the ratio of $[HONO]^{24m}$ to $[HONO]^{1m}$ is used with a shift of +15 min, but is not

6 shown. (b) $P_{unknown}^{24m}$ and (c) $P_{unknown}^{1m}$ are plotted against the photolytic loss rate of HONO at

7 24 m and 1 m above ground, respectively, colour codes mark the respective regimes of

8 "normal boreal" (green), "stressed boreal" (yellow) and "transported pollution" (grey). The

9 York linear fit (York et al., 2004) of $P_{unknown}^{24m}$ with L_{phot}^{24m} and $P_{unknown}^{1m}$ with L_{phot}^{1m} yields in

10 $P_{unknown}^{24m} = - (0.93 \pm 0.05)$ x $L_{phot}^{24m} + (0.9 \pm 14.2)$ x 10^3 molecules cm^{-3} s^{-1} and $P_{unknown}^{1m} = -$

11 (0.96 ± 0.08) x $L_{phot}^{1m} + (0.6 \pm 11.9)$ x 10^3 molecules cm^{-3} s^{-1}, respectively.

12