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Comment

## ***Interactive comment on “Development and application of a new mobile LOPAP instrument for the measurement of HONO altitude profiles in the planetary boundary layer” by R. Häsel er et al.***

### **Anonymous Referee #2**

Received and published: 23 October 2009

General Comments: The manuscript by Häsel er et al. describes the development of a modified LOPAP instrument for airborne measurements of nitrous acid on a Zeppelin platform. The manuscript is well written and presents highly interesting gradient measurements of HONO, although quite often no significant gradients were observed during daytime. The high HONO concentrations, which are still prevailing up to some hundred meters above the ground may contradict formation by proposed ground surface sources, which will be further evaluated in a forthcoming manuscript. The manuscript merits publication in AMT However, I have some problems with the weighting of the presentation of the development and characterization vs. the application of the new instrument. Especially, the intercomparison of LOPAP-Z with LOPAP-3 (see Fig. 4)

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shows some deviation (slope  $<1$ , intercept, low precision) and needs to be further evaluated. Since the same air mass was sampled by both instruments through one inlet the precision should be higher (ca. 1 % specified for both instruments). Previous inter-comparisons using the LOPAP-3 exhibited higher precision when the same air mass was sampled (e.g. Kleffmann et al., 2006). Some technical differences between both instruments may explain the (small) deviations, e.g. a longer glass inlet is used for the LOPAP-Z compared to the LOPAP-3. In addition, gas bubbles are not separated from reagent solution S1 after passing the stripping coil for the LOPAP-Z (see Fig. 3). This may increase sampling artefacts in the inlet and may increase chemical interferences. I would suggest a longer intercomparison exercise with a higher range of concentrations to exclude such artefacts. In contrast to the statement by the authors, using a common Teflon inlet (see page 2034, line 10 ff) is not a problem since sampling artefacts in Teflon lines, which are normally not used for the LOPAP will occur similarly for both instruments.

Specific comments Page 2028, line 18: The lifetime of HONO at noon during summer is much shorter than 20 min (around 10 min, e.g. 12 min for Forschungszentrum Jülich and even  $<10$  min for lower latitude).

Page 2028, 18-22: Some of the references used to demonstrate that HONO is an important OH source during the entire (...) were not well chosen. For example, in Aliche et al. HONO was below the detection limit during daytime and only the morning contribution could be calculated (the small daytime contribution was only estimated and not measured here). In addition, in the studies of Zhou et al. and Su et al. OH and J(HONO) were not measured and just estimated. However, for the quantification of the net OH production by HONO photolysis, both parameters are absolutely necessary.

Page 2029, line 7: LOPAP is the abbreviation of (LO)ng (P)ath (A)bsorption (P)hotometer.

Page 2029, line 17: Exchange “pumped” by “drawn”.

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Page 2029, line 28: Use “Teflon AF tubing” since normal Teflon cannot be used for this purpose.

Page 2030-2031: The different flow scheme (missing debubbler, see Fig. 3) should be added. In addition, the different inlet length of the gas inlets should be mentioned.

Page 2030-2031: Reference to Fig. 4 is missing between references to Fig. 3 and 5, change order of the figures.

Page 2033, 1-2: Was the dark signal of the spectrometer subtracted? Otherwise the response of the instrument is not linear with the concentration.

Page 2033, 3-4: Specify: the zero values are subtracted from the absorbance data. For details of the calculations a reference to Heland et al. could be added.

Page 2034, line 3: The sampling efficiency (ca. 95%) is much lower than that of the LOPAP-3 instrument, which is ca. 99 % for 1500 ml/min), although a similar stripping coil is used. This may be explained by high yield of NO<sub>2</sub> formed in the used HONO source and by the NO<sub>2</sub> interference of the instrument. HONO was formed here by mixing two solutions of H<sub>2</sub>SO<sub>4</sub> and nitrite in a washing bottle, which leads to decomposition of the initial high HONO concentrations in the aqueous phase. This can be avoided if both solutions are continuously mixed and exchanged in the washing bottle (see: Taira and Kanda, Anal. Chem., 1990, 62, 630-633). Was NO<sub>x</sub> also measured to exclude artificial underestimation of the sampling efficiency?

Page 2035, lines 22-23 and Table 1: The HO<sub>x</sub> measurements are also listed in Table 1 for ZEPTER1? May be in Table 1 the listed HO<sub>x</sub> set-up should be deleted?

Page 2036, lines 2-4: Some measurements during ZEPTER 1 started already at 4 h. Isn't this still during the late night? For ZEPTER 2, please specify “early night”.

Section 4: Although the topic of this manuscript is not the complete evaluation of the measurements, the missing gradients during daytime are highly interesting to the scientific community if the measured HONO concentration is higher than the PSS concen-

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tration. This would prove the existence of a strong daytime source of HONO in higher altitudes above the ground. Since the measurement data (OH, NO, HONO, J(HONO)) should be available, the authors may add just one sentence whether the HONO concentrations were equal (no extra HONO source, no gradient to be expected) or lower than the PSS (extra HONO source, strong gradient expected for the proposed ground sources).

Page 2038, line 7, “enormous variation ” during ZEPTEP 2: When comparing Fig. 7 (ZEPTEP 1) with Fig. 9 (ZEPTEP 2) the variation seems to be higher during ZEPTEP 1.

Page 2038, line 13-14, Figure 10: The similar frequency distribution between sunlight and dark conditions is to be expected caused by the dark measurement period, which was limited only to the early evening. Night-time formation of HONO is generally explained by ground surface sources, which will lead to the slowly evolution of gradients after sunset, with increasing HONO/NO<sub>x</sub> ratio during the night. Thus, for the higher altitudes (>50 m) HONO is expected to increase not directly after sunset but only later during the night (not measured here).

Page 2039, line 1-2: The statement given is only correct if HONO is higher than the PSS concentration (see above). In this case HONO is an important OH source, which should be measured. In contrast, if the concentrations are similar to the PSS, HONO measurements are not necessary and HONO concentrations can be easily calculated by gas phase chemistry in a rather simple model.

Page 2039, Appendix A: Since the tables belong to the main manuscript and since their content is already mentioned in the text the limited additional information given in the appendix may be added to section 3.2.

Page 2040-2042, reference list: There are numerous errors in the reference list, please check again. Generally, there are unknown numbers at the end of many references (e.g. Acker et al.: 2028; Aliche et al.: 2028, ...), which are probaly no page numbers?

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In addition, use subscript fonts for chemical formula (e.g. Kleffmann et al, 2007: HNO<sub>3</sub>, or Neftel et al.: HNO<sub>2</sub> and HNO<sub>3</sub>)

A few examples for other errors:

Acker et al: Meixner, F. X.; Strong daytime production...

Finlayson-Pitts and Pitts: should be year 2000

Harrison et al.: Harrison, R. M., Peak, J., D., Collins, G. M., issue 101 (not 30)

Different references to Kleffmann et al.: there is no order in the references

Kleffmann, 2007: ChemPhysChem, or European Journal of Chemical Physics and Physical Chemistry

Kleffmann et al., 2006: Lörzer J. C.

Kleffmann et al., 2007: Rodenas

Platt et al.: Harris, G. W., Winer, A. M., Pitts Jr., J. N.

Rohrer et al.: Brüning

Stemmler et al.: D'Anna, B. D.

Su et al.: Yu, Z. Y. is missing

Zhou et al.: Zhou, X. Dai, H.

Page 2043, Table caption 1: CL4 is not in the Table, delete in the caption

Page 2047, Fig 3 and corresponding text: Is the sampling unit protected against rain? In contrast to the LOPAP-3 there seems to be no rain protection shield. Sampling of rain droplets would strongly affect the precision of the instrument (dilution of the reagent + potential signal by nitrite in the rain water).

Page 2052, Figure caption 8: Should be October/November 2008...

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