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***Interactive comment on* “Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions” by J. Kleffmann and P. Wiesen**

J. Kleffmann and P. Wiesen

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Reply to Anonymous Referee #2

We are very grateful for the reviewer’s interest in our manuscript and the detailed comments and suggested corrections. The concerns raised by the reviewer are addressed below.

General comments:

As already specified in our reply to referee #1, we agree with the referee’s comment that the absolute interference signals measured by the LOPAP instrument cannot be transferred directly to other instruments. Based on all known intercomparison studies (see

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also below) and the differences in the HONO/NO_x ratio between the results reported here and other studies similar in remote areas, we also have explained in our reply to referee #1 that the interferences measured by the LOPAP technique are most probably only the lower limit of interferences of other chemical instruments. We will emphasise this in the revised manuscript. In addition, below and in the revised manuscript we will comment in more detail to the two intercomparison studies mentioned by the referee, which are in perfect agreement with our conclusions. The referee also asked for more quantitative description. We will take this into account in the revised manuscript as far as possible. However, some of the referee's suggestions could not be answered since they are unknown and/or may not improve the manuscript. This point will be addressed below in the section "specific comments". We also regret that there are still several spelling and grammatical errors in the manuscript. The revised manuscript will be corrected by a native English speaking person accordingly.

Specific Comments:

Acronyms:

All acronyms will be explained when first used in the revised manuscript.

Abstract line 3+5.

In line 5 we have specified the lower limit concentration of <0.5 ppt and not <5 ppt. The reason, that the lower limit is higher than the specified DL (0.2 ppt) was caused by the extremely high relative interferences observed during the campaign in channel 2, which caused the errors of the differences between the two channels of the instrument (= [HONO]) to increase. For these conditions, we had to subtract for example, 3.5 ppt (channel 2) from 4 ppt (channel 1; each signal with the noise from the LOPAP instrument and the atmospheric variability) to get a HONO concentration of 0.5 ppt. In contrast, the detection limit was determined during zero air measurements, with no signals in both channels and the error only given by the signal noise of both channels.

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Abstract, line 7:

The "very low" night-time concentrations are quantified in section 3.1 and in Fig. 2. However, in our opinion in an abstract not all details should be explicitly mentioned, otherwise one should also report in the abstract numbers for the daytime values, variation of the HONO/NO_x ratio, etc., which are of similar importance for the reader. In addition, an average night-time concentration of 3.5 ppt (see section 3.1) is considered to be very low (there are not many lower measurements available even under polar conditions, which may be considered as more "remote"...).

Page 3501-3502:

As explained in detail in the last paragraph on page 3503 and in Fig. 1, the detection limit of the LOPAP instrument is 0.2 ppt, which we consider as "very, if not extremely sensitive".

To our knowledge, the liquid phase rate constants of the neutralization of HONO to NO⁺ and the reaction of NO⁺ with sulfanilamide are not known (most probably nearly diffusion limited...). Thus, "very fast" cannot be specified. However, the reaction is so fast that the uptake of HONO in our sampling solution is much faster than the uptake of HNO₃ on water in the same coil (the reason why we had to use a 10-coil sampler in our HNO₃-LOPAP (J. Atmos. Chem., 2007, 58(2), 131-150), whereas a 4-coil sampler is used in the HONO instrument). We will add this information to the revised manuscript.

The expression "very short" is already exactly quantified in the manuscript, namely 17 cm, 2 mm i.d.

Page 3506, lines 15-17:

Will be corrected in the revised manuscript.

Page 3507, line 3:

As specified in the experimental section the sulfanilamide concentration is 10 g/l,

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whereas the highest concentrations of HONO were 50 ppt, which easily translate into molar concentrations of 0.063 mol/l and 1.5×10^{-8} mol/l, respectively (for a liquid flow of 0.2 ml/min and a gas flow of 1.5 l/min, see experimental section). Thus, the excess is more than 6 orders of magnitude, which we consider as a "very high excess".

Page 3507, line 10:

During a photosmog experiment using toluene, n-butane, ethene, NO_x and natural sunlight (see Kleffmann et al., 2006) many hundreds (if not thousands...) of products will be formed, which we consider as "very complex conditions". It is impossible to specify/quantify all the compounds formed during the degradation of this mixture.

Page 3508, par. 1, general:

We would like to thank the referee for the details of the study of Keene et al., 2006, which are, however, unfortunately not specified in the published paper. For some details, the referee refers to the study of Keene et al., 2004, however details for HONO are only discussed in the 2006 paper, see page 6, left column of the 2006 paper: "...those (...performance characteristics...) for HONO are discussed below.". Since HONO is not discussed in the Keene et al. publication from 2004 and the intercomparison is only explained in the publication from 2006 without providing more details of the experimental part of the intercomparison study, obviously we have only considered the experimental section of the 2006 paper as valid for the reported HONO measurements.

Page 3508, par. 1, inlet losses:

In addition, it is not obvious why losses of HONO in the inlet should be not a problem under marine conditions, for example by uptake of HONO on deposited alkaline sea spray in the inlet. Inlets always cause problems (see for example Keene 2006, page 6, right column: "... via artefact (...inlet...) reactions [e.g. Zhou et al., 2002].") This is the reason why no inlet line is used in the sampling unit of the LOPAP.

Page 3508, par. 1, conversion of HONO to HNO₃ in the instrument:

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Why should HONO not be converted into HNO₃ under marine conditions, but under biomass-burning conditions? If HONO is converted, for example by reaction with dissolved O₂, which is a well-known problem for very low nitrite concentrations, this should always happen in the instrument. The HNO₃ concentration level (only this corresponding detail can be found in Keene et al., 2004 and Fischer et al., 2006...) will not influence this problem! The information that nitrate was not added to nitrite for the calculation of the HONO concentration during the intercomparison is not given in this paper. In addition, it is not mentioned in the Keene et al. publication from 2006 that the mist chamber solution was analyzed immediately and not some hours later as specified in the experimental section of this paper. However, what means "immediately"? If nitrite is oxidized completely in a few hours (see Keene et al., 2006) this conversion will also appear within the first several minutes, where the highest conversion rates will occur. Therefore, nitrite originally in the mist chamber solution (see Keene et al., 2006: "...presumably (...) from HONO dissolution...") will have been underestimated, at least to some extent. In this case, the HONO data by the mist chamber would have been even higher during the intercomparison, if nitrite would not have been lost (see below).

In conclusion, caused by:

- a) the incomplete testing (Keene et al.: "...performance characteristics of the MC-IC technique for HONO have not been rigorously characterized."),
- b) the negative artefact by nitrite to nitrate oxidation (see above)
- c) the unknown inlet problems (see above),
- d) since almost half of the data points were below the detection limit of the DOAS
- e) the Keene et al., 2006 statement: "...are considered semi-quantitative..." and
- f) since no intercomparison data are shown,

we originally did not consider this paper for the discussion of recent intercomparison studies. However, we were advised to include this paper in the pre-review process

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of ACPD. Thus, let us assume the numbers given in the Keene et al. paper to be "quantitative", i.e. the slope $MC/DOAS = 1.2$ and the intercept $MC (DOAS=0) = 49$ ppt to be statistically significant. Using these numbers, the results from the Keene et al. intercomparison would be in perfect agreement with our conclusions that chemical instruments are working reliably for high HONO concentrations, but strongly overestimate low HONO concentrations. For example, for 500 ppt HONO the MC/IC instrument would measure 650 ppt, a deviation of 15 %, which may be acceptable, whereas for 50 ppt HONO the MC/IC instrument would measure 110 ppt, an overestimation of more than a factor of two. For conditions prevailing at the South Pole and average HONO concentrations of 6 ppt (see Liao et al., 2006 compare also our study at Jungfraujoch: 7.5 ppt), the MC/IC instrument would measure 50 ppt, a factor of 8 higher, which is in line with the overestimation of a factor of seven observed by Liao et al., 2006. In addition, since at least some of the nitrite may be lost in Keene et al. intercomparison study (see above), the "true" MC/IC value would be even higher than the numbers calculated. The calculated deviations would be again higher than the interferences measured and corrected by the LOPAP instrument for similar HONO levels (see Fig 7 from Kleffmann et al., 2006 and Fig. 5 from this study). Thus, even if we take the numbers from the Keene et al. paper as statistically significant, this would be another nice example, why we consider that the interferences measured by the LOPAP have to be taken only as a lower limit of overestimations of HONO concentrations measured by other chemical instruments.

Page 3508, lines 20-21:

The referee asked for more details of the intercomparison of the DOAS and the HPLC system during the NITROCAT campaign in Rome, a EU-funded project, which was coordinated by our group. This would, however, go beyond the scope of a simple listing and discussion of major results from recent intercomparison studies, but which will be given now below:

Significant DOAS values: The detection limit of the DOAS was almost always below

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the typical daytime values of 150-300 ppt (mean DL = 84 ppt). Thus, almost all values are significant.

Description of the daytime deviations observed: Only for the first two days (shown in Acker et al., "very good agreement"...) and for some few daytime periods later (in sum, a few hours), the HPLC was similar to the DOAS (but not systematically lower!). On all other days, the HPLC was significantly higher than the DOAS during daytime. There are several days, during which the DOAS HONO signal was continuously factors lower than the HPLC signal during daytime (statistically significant). In addition, when all HPLC data were plotted against the DOAS data the regression analysis yields a slope of (0.92+/-0.03), an intercept of (0.20+/-0.03) and an $R^2 = 0.64$. This means, that for high concentrations there was reasonable agreement between both instruments (for example, at 2 ppb DOAS the HPLC measured on average also 2 ppb). However, during daytime the HPLC measured significantly higher values than the DOAS (for example, at 150 ppt (DOAS) the HPLC measured on average 330 ppt). I hope that these details, which will be partly added to the revised manuscript, will help to better justify our statement. Again the LOPAP correction would be lower than the deviation of the HPLC and the DOAS, for other examples see: reply to referee #1).

Page 3509, lines 4-7:

In contrast to the referee's statement, we are convinced that we have clarified that there is to date no intercomparison available, which conclusively shows that interferences are not (!) a significant problem of other chemical instruments measuring HONO. In contrast, available remote/polar HONO/NO_x data indicate a strong overestimation of HONO at low concentrations. For example, a published 100 % HONO/NO_x ratio is implausible if not impossible, caused by the fast photolysis of HONO (ca. 10 min lifetime) leading to NO_x formation (having a much longer lifetime). In addition, the intercomparison studies demonstrate that the deviations published for chemical instruments compared to spectroscopic techniques are even higher than the average interference corrections of different LOPAP campaigns at similar HONO concentrations (compare

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with Fig 7 from Kleffmann et al., 2006 and Fig. 5 from this study). We are convinced that this conclusion is of crucial importance for the manuscript in order to help colleagues in the critical assessment of former published HONO data. However, we will emphasise in the revised manuscript that the absolute corrections of the LOPAP instrument represent only a lower limit of interferences of other chemical HONO instruments.

Page 3509, lines 10-15:

We will change this formulation according to the referee's suggestion in the revised manuscript.

Page 3509, last line:

We observed in both studies an inverse dependency of the relative interference correction with the HONO level. To show how "excellent" they fit together, one has to plot all average interference data against the corresponding average HONO data (see Fig. 7 from Kleffmann et al., 2006, as an example). If this is done, the data from the present Jungfraujoch manuscript are in perfect agreement with other campaigns during which LOPAP instruments have been used. If necessary we could add such a figure to the revised manuscript.

Page 3510, line 4:

Will be changed in the revised manuscript

Page 3510, lines 10-11:

This is the major conclusion of the manuscript and we would like to leave this sentence unchanged (see the discussion above).

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3497, 2008.

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