

We thank Anonymous Referee #2 for his/her comments and interest and for recommending our paper for publication. Below are our replies, given the same numbers as the comments.

1. We respectfully disagree with Referee#2 that the data sources were biased. To the best of our knowledge, this is the first study where a large number of HONO measurements are intercompared in detail. The current study employs a HONO/NO_x parameterization based on data from 15 field measurement campaigns around the globe (see Table 1 and Fig. 3) performed during the last decade under very different seasonal and geographical conditions. They range from VOC-sensitive conditions, mainly in urban polluted areas (e.g., Santiago, New York, Milan) to NO_x-limited conditions, mainly in rural (e.g., HOxComp, PRIDE-PRD2006) and remote (DOMINO) areas as also mentioned in sec. 2.2, pages 12891-12892. Thus, this parameterization is not limited only to urban high NO_x conditions but represents an overview of HONO measurements over a wide range of atmospheric conditions.

For the study of Acker et al. (2006) at Hohenpeißenberg, only HONO/NO₂ ratio is provided and not HONO/NO_x, so the comparison here is not accurate. In their study, HONO was measured by a coupled wet denuder sampling/IC technique (Acker et al., 2006) with average daytime HONO/NO₂ of 0.089 but with very poor correlation between HONO and NO₂, $r^2 = 0.016$ (Acker et al., 2006). This HONO/NO₂ ratio may correspond to a HONO/NO_x of about 0.07 (considering NO₂/NO_x of about 0.8, see Table 1). In addition, we could not determine or find the mentioned value of HONO/NO_x of 0.30 in this reference. For the rural site in New York state (Zhou et al., 2002), HONO was measured by aqueous-phase scrubbing and HPLC analysis with HONO/NO_x ratio ranging from <0.01-0.3 with median and average HONO/NO_x ratio of 0.06 and 0.07, respectively, thus not from 0.07 to 0.3 as mentioned in the comment. At the summit of Whiteface Mountain, New York, HONO was measured using also the aqueous-phase scrubbing and HPLC analysis, with a very high daytime average HONO/NO_x ratio of about 0.33 under rather low NO_x levels (< 0.25 ppbv) (Zhou et al., 2007). In contrast, at Jungfraujoch, the mean HONO/NO_x ratio was measured using the LOPAP technique being only 0.046% (Kleffmann and Wiesen, 2008).

In the most recent of these mentioned studies (Kleffmann and Wiesen, 2008 and references therein), these previously very high HONO/NO_x ratios (observed using wet-chemical techniques other than LOPAP) were explicitly investigated and were

related to uncorrected chemical interferences leading to high measured HONO levels, especially under very low HONO and NO_x levels. Under these conditions HONO levels are quite low (daytime average mixing ratios of 100, 60, 46, 7.5 pptv in Hohenpeißenberg; rural site in New York City; Whiteface Mountain, New York; Jungfraujoch, respectively) and therefore their values can be high-biased by even very small interferences which can reach >100% of the observed values (Kleffmann and Wiesen, 2008 and references therein). Therefore, the highest average HONO/NO_x ratio of 0.33 measured at the summit of whiteface Mountain, New York under very low NO_x values (<0.25 ppbv) can probably be related to HONO interferences (Kleffmann and Wiesen, 2008). As also explicitly shown in the study of Kleffmann and Wiesen (2008), the LOPAP instrument has the advantage of having a two-channel system that corrects for such interferences and thus is more suitable for such HONO measurements under clean conditions.

More recent studies acknowledged this problem and are either correcting (Su et al., 2008) for such interferences or modifying the technique to minimize them (Lu et al., 2010; Ren et al., 2010; Zhang et al., 2012). For example, in the study of Su et al. (2008) at PRIDE-PRD2004, which data is used in the current study, they showed that measured HONO by the wet denuder/Ion Chromatograph (WD/IC) system can overestimate HONO by a factor of 2 compared to LOPAP due to HONO formation inside the sampling inlet of this instrument (in LOPAP, there are no sampling lines at all). Therefore, they applied an empirical correction for this uncertainty. Lu et al. (2010) compared also the WD/IC to LOPAP and found that WD/IC significantly overestimate HONO, reaching a factor of 3, compared to LOPAP, thus used the LOPAP data as model constraint. Most recently, Zhang et al. (2012) modified the aforementioned wet-chemical system to avoid sources of interferences by replacing the organic solvents as mobile phase in the HPLC (major source of interferences) by a Long-path photometric technique (similar to LOPAP).

Thus, these mentioned very high HONO/NO_x ratios are due to significant uncorrected interferences associated with these HONO measurements under these very low NO_x conditions using wet-chemical techniques (other than LOPAP); therefore, they should not be included in our data evaluation. In our study, measurements using wet-chemical techniques other than LOPAP were restricted to high NO_x polluted areas (in New York City and PRIDE-PRD2004 (this location is rural but influenced by polluted air masses), while for low NO_x rural (e.g., HOxComp, PRIDE-PRD2006)

and remote (DOMINO) regions, only measurements using the LOPAP technique were considered. Under high NO_x conditions, the relative contribution of these interferences is relatively low and therefore other wet-chemical techniques can be considered in addition to LOPAP and DOAS (Kleffmann et al., 2006; Kleffmann and Wiesen, 2008). Therefore, it is not necessary for low NO_x remote areas to have a specific, i.e. high HONO/NO_x value, as these values were probably measurement artefacts. For example, in the DOMINO campaign (rural to remote site, HONO was measured by LOPAP), the average daytime HONO/NO_x ratio was only 0.02 while for polluted high NO_x conditions in Santiago_S, it was 0.04 (see table 1 and Fig. 3). In addition, a low NO_x rural site can be influenced by high NO_x polluted air masses (e.g., PRID-PRD2004), therefore, it is neither recommended nor possible to derive one average HONO/NO_x ratio for low NO_x and another ratio for high NO_x . Furthermore, the correlation shown in Fig. 3 of all measurement 15 campaigns under different atmospheric conditions reveal only one slope of 0.02.

Therefore, the data sets used in the current study represent a comprehensive overview of all HONO measurements with sufficient accuracy (i.e., avoiding known measurements artefacts as mentioned above). Furthermore, in low- NO_x environments (rural or remote), which are also well represented in our study, HONO photolysis during daytime does not have any impact on HO_x and secondary oxidation products owing to the low NO levels, under which HO_x recycling is not efficient as discussed in detail in sec. 3.3.

The following statement has been added on line 27, page 12894 to account for this issue:

“It is worth mentioning that HONO measurements under very clean conditions, using wet-chemical techniques (other than LOPAP) have been reported to be biased by uncorrected interferences leading to artificially high HONO/NO_x ratios (Kleffmann et al., 2006; Kleffmann and Wiesen, 2008; Su et al., 2008, Lu et al., 2010; Zhang et al., 2012). Recent studies acknowledged this problem and corrected for these interferences (e.g., Su et al., 2008) or modified the technique to minimize them (e.g., Ren et al., 2010; Zhang et al., 2012). Under high NO_x polluted conditions this problem is less pronounced (e.g., Kleffmann et al., 2006; Kleffmann and Wiesen, 2008). In the current study, only HONO measurements by LOPAP are considered for low NO_x conditions while for high NO_x conditions,

LOPAP, DOAS and aqueous-phase scrubbing and HPLC or ion chromatography (IC) analysis techniques are used.”.

2. The HONO concentrations over the North Atlantic and North Pacific oceans are within the ranges of 0.001 to 0.01 ppbv; these are not significant (please note the logarithmic scale in Fig. 11). These simulated very low HONO levels are quite realistic due to the presence of low NO_x emissions (i.e., NO+OH→HONO and HONO emissions) from air- and ship traffic in these regions (Jöckel et al., 2006). These HONO levels obviously lead to a small enhancement in OH levels (HONO+hv→OH+NO) within the range of 5-15 %, which are quite low compared to up to about 800% enhancement in polluted regions (see Fig. 15 and please note the logarithmic scale). For O₃, no enhancements can be seen in Figs. 14 and 15 in these regions (contrary to the comment) because of the very low NO levels (NO-limited conditions, see sec. 3.3).

3. The model vertical resolution is L31 (up to ~30 km height) which corresponds to a height of the first layer of the vertical grid centred around ~30 m above the ground, depending on the topography. As discussed in sec. 2.3 (and shown in Fig. 2), measured HONO and NO_x levels on the ground show clear gradients. However, owing to the almost stable vertical HONO/NO_x ratio (i.e., HONO/NO_x ratio does not show a vertical gradient as shown in sec. 2.3), the simulated HONO levels can be adequately calculated. In fact this is the main reason why we used HONO/NO_x (constant vertical values) and not HONO/NO₂ (varying vertical values) as discussed in sec. 2.3 and shown in Fig. 2. For most of the field measurement campaigns HONO is typically measured at about 10 m (e.g., Sörgel et al., 2011; Villena et al., 2011; Elshorbany et al., 2012) to 20 m (e.g., Wong et al., 2012). Therefore, the height of the first layer in the model is not significantly higher than in typical field measurements. In addition, in HONO gradient measurements at 16 to 70 m height (Volkamer et al., 2010), 6 to 53 m height (Vellina te al., 2011) and at 20 to 300 m height (Wong et al., 2009), HONO was only reduced by about 50-60% at the highest respective altitude. Therefore, only minor differences (if any) are expected due to the first layer height of about 30 m. Furthermore, we have mentioned in page 12903, lines 13-15 (when comparing model simulation to measurements) that these

comparisons are approximations owing to the coarse model resolution compared to the measurements.

In response to referee#2's suggestion, we show simulated HONO mixing ratios, averaged over the northern hemisphere (30°N to 50°N) during summer and winter within the first 1200 m above the ground (Fig. 12, revised manuscript) and an explanation has been inserted on line 10, page 12903.

4. Eq. (5) and Eq. (6) are used to calculate HONO levels in sectors B (sunrise to mid-noon) and C (mid-noon to sunset), respectively. Both sectors B and C represent the daytime sector (sunrise to sunset), for which HONO concentration dependencies (on NO_x and $j(\text{NO}_2)$) are also investigated in sec. 3.2.2, Fig. 6 and Fig. 7 (compared to sector B, right panel) as suggested by the referee. Owing to the different duration of the daylight hours in each campaign (i.e. different geographic locations and seasons), it is not useful to determine a unified specific time range, say from 9:00 to 15:00. Owing to the different contribution of HONO sources during both time sectors (for sector B, mainly $[\text{HONO}]_{\text{pss+emissions}}$ (page 12897, line 15 on) and for sector C, mainly unidentified sources (page 12898, line 15 on), see sec. 3.2.2), both sectors have been further treated separately in more detail in order to investigate their HONO dependency in each sector, see sec. 3.2.2 and sec. 3.2.3.