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Atmospheric
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Discussions

Interactive comment on “Intercomparison of nitrous acid (HONO) measurement techniques in a megacity (Beijing)” *by* Leigh R. Crilley et al.

Anonymous Referee #1

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This study reported an inter-comparison exercise between HONO measurements performed by multiple instruments. The results show that despite of good agreement on the temporal trends, the wet chemical methods consistently higher than the BBCEAS systems by between 12 and 39%. The reason for the divergence was not clear and the authors have speculated and discussed the potential influence of instrument locations.

HONO is one of the most important precursors of OH radicals. Reliable measurements of HONO are key to understand its origin and role in the atmospheric chemistry. This study provides a great dataset to examine the performance and potential problems of HONO detectors in an atmosphere subject to strong anthropogenic influences. Overall, I think it is a nice study and would recommend its publication with revisions. My main concerns are that (1) the authors may put too much weight on the contribution/discussion of spatial heterogeneity. Do you think that you may see an reverse relation (wet chemical concentration < BBCEAS) if you exchange the sampling locations? (2) the discussion about the daytime difference seems to be missing or mixed in the discussion. The 12% to 39% may not reflect the real difference up to several folds during daytime, the most relevant periods for the photochemical reactions. Please find detailed comments below.

Comments:

Page 1 line 36 “with the wet chemical methods consistently higher than the BBCEAS systems by between 12 and 39%.” Is it the case for daytime, night time, I saw 100%?

Page 1 line 38 “The causes of the divergence in absolute HONO concentrations were unclear, and may in part have been due to spatial variability, i.e. differences in instrument location / inlet position.” Did you check the concentration of other trace gases aerosols, T, RH, etc?

Page 2 Introduction “contributing up to 40% of the OH budget in London (Lee et al., 2016).” The authors may consider referring to its contribution to the primary production of OH, where you can find more references (e.g., Kleffmann et al., GRL, 2005; Acker et al., GRL, 2006; Su et al., JGR, 2008) including measurements in Beijing (Yang et al., 2014).

Page 2 Introduction “There are a number of known sources of HONO including direct emissions, heterogeneous reactions, homogenous gas-phase reactions, biological processes and surface photolysis (see reviews by (Kleffmann, 2007;Spataro and Ianniello, 2014).” When talking about different sources, I’d suggest crediting the original research rather than exclusive referring to reviews.

Page 2 line 14 “Positive artefacts can occur in inlet lines, as HONO is easily formed through heterogeneous reactions on wet surfaces (Zhou et al., 2003).” The study of Zhou is not about the heterogeneous reactions on inlets. It is discussing the formation of HONO and NOx from photolysis of HNO3. Concerning the artefacts in inlet lines, you could refer to the studies of Zhou et al. (GRL,2002) and Su et al. (AE, 2008). The LOPAP style instruments have an outdoor sampling unit without additional inlet. Is this the case for the two wet chemical analyzers used here? What's the length of inlet of the other unspecified instruments?

Page 8 line 26 "The co-efficient of variance (CV) is defined as the standard deviation divided by the mean and is used to compare the relative degree of variation between datasets." The authors should explain how to calculate CV explicitly because the mean and deviation can be calculated for an individual dataset. My understanding is that here you calculate CV of data from different instruments at each time step and it is better to clarify this

Page 9 line 5 "the applied reference NO2 spectrum might contain absorption signatures from HONO. This would result in a higher NO2/HONO ratio retrieved from the BBCEAS compared to ambient air, and consequently reporting a low HONO mixing ratio (Kleffmann et al., 2006). However, the Voigt et al (2002) NO2 cross-section, used by both BBCEAS instruments, has previously been shown to have negligible HONO absorption structures (Veitel, 2002)." This part of discussion is not optimal. On one hand, you stated that the applied reference spectrum might be problematic. On the other hand, you referred to Veitel et al. 2002 saying that it is negligible. Actually, this is also the information provided by Kleffmann et al. (2006). Since you were using the one from Voigt et al., it should solve the impurity issue as suggested by Kleffmann et al. (2006). I'd suggest a reformulation of this part.

Page 9 line 15: "The systematic error for each instrument can be calculated by normalised sequential difference (NSD) according to Eqn 1 (Arnold et al., 2007)" The authors should better explain equation 1. What's the meaning of t and t+1, is it time? You later used i, j, what's their difference? Why it reflects a systematic error? People may have different ways to define a systematic error vs a random error. But the fact that BHAM was always higher than CAMB for me is a clear evidence for systematic

errors.

Page 10 line 2 "The ND was evaluated as function of wind direction and measured HONO concentration (Fig 3), to explore if ambient concentration or spatial heterogeneity could explain the disagreements." Do you have other parameters (e.g., SO2, O3, NOx, etc) that have been measured in different containers? A comparison of these parameters may give you a better idea about the spatial heterogeneity, and help to disentangle it from the other effects. Besides, the spatial heterogeneity and HONO concentration might not be the only reasons for the observed differences. Artefacts and intrinsic limitation of individual methods could also results in different kinds of disagreement. These, however, were not discussed in this study. Do you consider these as minor issues here?

Page 10 Section 3.1.4. Here the authors investigated the concentration dependence of instrument agreement through comparison of slopes between the whole dataset and a subset of data. Can you give more details why you were expecting a concentration dependence, or what could lead to a concentration dependence? Do you think the detection limit would be an issue here? This can be easily checked by exclusively comparing data above the threshold. I also have some technical questions: (1) how did you conclude "the observed slopes between the BHAM15 ICCAS-AIOFM at low concentrations (<2 ppb) were similar to those .."? Because according to the confidence interval in Table 2 and 4, these slopes could be significantly different; (2) what's the criteria of choosing 2 ppb as the threshold, will the results change if you take other values, e.g., 0.5 ppb? A more straight forward way to investigate the concentration dependence would be directly plot the difference or normalized difference against the concentration. HONO concentration also has a strong diurnal cycle, with a minimum around noon time with active photochemistry and temperature. The concentration dependence of bias might also be caused by a diurnal cycle of the interference signals as discussed in Su et al. (AE 2008). Can you check if the difference in your study also has a prominent diurnal cycle?

Page 10 line 32: “However, when comparing the between the two different instrument types (wet” Some words missing?

Page 11 line 5 “this may reflect spatial variability in HONO concentrations as some of the instrument inlet locations” I am not convinced about the role of spatial variability. Because how to maintain a large gradient of HONO in 3 meters? Could you make some estimation about the heterogeneity of the source/driving force by taking a typical turbulent diffusion coefficient?

Page 12 line 30 “We note that the two-channel stripping coil used in the sampling inlet for both the BHAM and ICCAS “ Did you compare the signal of the second channel of the two-LOPAP style instruments? This channel is supposed to provide information about most inference species. Detailed analysis (e.g., correlation study with different nitrogen-containing compounds, or of it diurnal variation) may give you a better idea of the interference problems. Such a comparison can also be used to check the performance of both instruments and spatial heterogeneity.

Figure 2: The CV has a unit of “%”. Is it correct? A CV of 1% is too small according to Fig. 1.

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