

# ***Interactive comment on “Exploration of the atmospheric chemistry of nitrous acid in a coastal city of southeastern China: Results from measurements across four seasons” by Baoye Hu et al.***

## **Anonymous Referee #2**

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The manuscript “Exploration of the atmospheric chemistry of nitrous acid in a coastal city of southeastern China: Results from measurements across four seasons” by Hu et al. provides observations and analysis of compounds important for improving understanding of tropospheric chemistry. The topic is important to many readers, and this study is closely related to a large number of papers that try to understand atmospheric HONO abundance and its impact on oxidants. The writing is clear, and the observations are sufficiently unique and comprehensive to provide new insights.

Regrettably, the utility of the manuscript is compromised by the omission of many im-

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portant experimental details, such that the context and relevance of the measurements reported here cannot be ascertained. Additionally, there are several analyses that are incomplete or difficult to understand. Consequently, I cannot recommend this paper for publication. I do hope that these measurements will receive further examination and that a paper will be written that considers some of the suggestions below.

The methodology section is far too brief, and many critical details are absent. The reference (Duan et al, 2018) that describes the HONO instrument notes the importance of characterizing HONO transmission and production in inlets. There is no mention of any of the sampling inlets. NO<sub>2</sub> readily converts to HONO on surfaces, but there is no way to assess the importance of this artifact without a thorough description of inlet length, material, flow, etc. Are filters used on the IBBCEAS to remove ambient aerosol, as in Min et al., 2016? If so, how often are they changed? What are the uncertainties for the aerosol and NO measurements? It would be helpful to show how the IBBCEAS and TEI NO<sub>2</sub> measurements compare. Line 105 says the TEI "might actually include other active nitrogen compounds". Did it? This assertion should be tested, or at least referenced.

The measurement site isn't described adequately. The paper notes that a coastal location, land/sea breeze effects, vehicle exhaust emission, and contributions from diesel traffic are important for understanding HONO abundance, but none of these contributions are detailed here. The conclusion states that site was surrounded by expressways, but these are not detailed in the body of the text. How close are the expressways? Are there diurnal traffic patterns? Figure 1 gives a map, but it does not have sufficient detail to understand the sampling location. The figure should show latitude on an axis, clearly identify land and water, show major roads. And the map should use km rather than miles. The meteorology must be described. Is there a land/sea breeze effect here? What is the mixed layer height? Is the top of the building always within the mixed layer? I expect some nighttime measurements are capturing a residual layer of pollution that may have been processed for longer periods. How large

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is the city, and what is the proximity of soils and tall buildings (proposed sources of HONO)? The motivation for this paper is that coastal cities have been undersampled, but none of the characteristics important to this coastal location are described.

Critical ancillary measurements are not adequately reported. What are the Ozone levels at night? The paper reports the average ozone for the entire study, but this doesn't reveal whether ozone is titrated at night, whether there is large ozone production during the day, and the photochemical environment of the measurement location. What is the temperature at this location? Figures 2 and 6 show that the length of day is the same for all seasons, but this can't be right. On line 99, please describe what you mean with  $_R$  and  $_M$  in the photolysis rate constants.

Several of the interpretations are difficult for me to understand and require further analysis. For example, line 264 says "It is hoped that HONO is in the photostationary state. . . .", and from there, all calculations assume that is the case. The PSS assumption needs to be carefully examined. An analysis of measurements from a similar height on top of a building in Houston show that the PSS assumption may not be correct (Lee et al, Urban measurements of atmospheric nitrous acid: A caveat on the interpretation of the HONO photostationary state, JGR 2013). The Lee et al paper shows that the PSS assumption needs to be carefully examined to quantify the strength of an unknown HONO source. And this is especially true for measurements that are adjacent to major expressways. Table 2 shows fresh vehicle plumes measured during midday with HONO/NOx comparable to nighttime measurements, which may suggest that these plumes are not in PSS. What is HONO/NOx (PSS) for the daytime plumes in Table 2?

The HONO production rate from unknown sources reported here is gigantic: 14.78 ppb/h in summer, when it accounted for nearly all HONO production. This number should be compared with previous reports. Have such high values every been reported before? Ryan et al (referenced here) report 1 ppb/hr, and some studies have shown that summer daytime HONO and HONO/NOx can be explained without invoking any unknown source (Lee et al, Urban measurements of atmospheric nitrous acid: A

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caveat on the interpretation of the HONO photostationary state, JGR 2013; Neuman et al., HONO emission and production determined from airborne measurements over the Southeast U.S., JGR 2016).

Several of the figures are difficult to understand. What are the red lines and dashed lines in figure 8? The logarithmic fits should be described, as they don't appear to encompass the data. It appears that the data could be just as easily fit with a line. What is the color scale on the right? What are the green squares in Figure 10? It would be helpful to keep a consistent color scale for the seasons. All of the figure captions should be expanded to explicitly identify every symbol and line shown on each figure. Labels and units must be included for every axis and colorscale (these are missing on figs 1, 2, 3, 6, 8).

I have trouble making sense of the concluding lines of the abstract and conclusion. The conclusion ends (lines 448-450) by stating that HONO provides an OH radical source (4.31 ppb/h) an order of magnitude greater than its concentration (0.66 ppb). I don't understand the comparison of a production rate with a concentration. The order of magnitude increase is also mentioned in the previous section, but I cannot see where this value comes from. The last line of the abstract states the study "draws a full picture of the sources of HONO..." But the vast majority of sources are unidentified. A more accurate statement might be that the HONO observations here do not identify the processes that determine HONO chemistry.

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