

## ***Interactive comment on “Evaluating the measurement interference of wet rotating denuder-IC in measuring atmospheric HONO in highly polluted area” by Zheng Xu et al.***

### **Anonymous Referee #1**

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This study systematically evaluates the interferences of atmospheric trace gases on HONO measurements by using the prevailing WD/IC technique through comparison with the LOPAP technique that is currently believed to be one of the reliable techniques for HONO measurements. The results and conclusions of the manuscript seem to be convincing and the method established for correcting HONO concentrations measured by the WD/IC technique is useful to calibrate the large database measured in the past and ongoing data. This reviewer recommends the manuscript to be published in the journal after considering following specifics:

1. Lines 49-52, the chemical method of stripping coil-ion chromatograph is suggested

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to be included, e.g., Cheng et al., 2013, J. Environ. Sci. (Chinese) 25, 895-907; Xue et al., 2019, Science of the total Environment, 646: 187-195; 659: 621-631. 2. 2.2 Instrumentation: The length of inlet tube for both the MARGA and LOPAP is suggested to be mentioned because serious interference of the inlet tube may be important as you mentioned in the introduction. 3. Lines 171-175, the description of the two sentences is not clear, and suggested to be rephrased as “The average diurnal variations of HONO marga and HONO lopap, as shown Figure 1b, HONO marga /HONO lopap ratios were higher at night, and especially in the morning, which were different from the results of Muller et al. (1999) who found the remarkable overestimation of HONO by WD/IC usually occurred during daytime.”. 4. Lines 175-177, “Meanwhile, the correlation between the HONO concentrations measured by WD/IC and other measured HONO concentrations varied in different studies.” is suggested to be replaced by “Meanwhile, the correlations between the HONO concentrations measured by WD/IC and by another techniques varied in different studies.”. This sentence seems to be meaningless, can be deleted. 5. Lines 177-181, “In our study, the slope of HONO lopap to HONO marga was approximately 0.57, with a correlation coefficient  $r^2=0.3$ . Combined with the limited comparison study on HONO concentrations measured by a WD/IC instrument and LOPAP (Lu et al., 2010; Ramsay et al., 2018), the slope at the four sites varied from 0.32 to 0.87. The large variation may indicate that the performance of WD/IC in the measurement of HONO is environmental dependent” is suggested to be replaced by “the slope of HONO lopap to HONO marga measured by this study was approximately 0.57 (with a correlation coefficient of  $r^2=0.3$ ) which was within the large range of 0.32-0.87 reported by the limited comparison investigations on HONO measurements using a WD/IC instrument and LOPAP at four sampling sites (Lu et al., 2010; Ramsay et al., 2018). Such large variation of the slopes at the different sampling sites may indicate that the performance of WD/IC in the measurement of HONO is environmental dependent”. In addition, a brief introduction of the difference for the environments at the different sites is needed, or the conclusion is farfetched. 6. Lines 185-187, “As the major precursor of HONO, the heterogeneous reaction of NO<sub>2</sub> on the sampling

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tube or aerosol may introduce the artificial HONO” should be “As the potential source for HONO, the heterogeneous reaction of NO<sub>2</sub> on the sampling tube or aerosol may introduce the artificial HONO”. 7. Lines 192-194, the phenomenon described by “Compared to HONOlopap, HONOmarga was significantly higher at a high concentration of SO<sub>2</sub> and had the opposite trend at a high concentration of ammonia” is inconsistent with Figure 2 and the following discussions. According to the illustration of Figure 2, HONOmarga was much higher than HONOlopap under lower SO<sub>2</sub> concentrations and higher NH<sub>3</sub> concentrations, and vice versa. 8. Lines 230-231, are the 13 samples collected from the atmosphere, or specially prepared? It is difficult to understand the large range of pH values (from 0-14) for actual air samples. The authors are suggested to present the detail information about it. The reliability for calculating the pH of solution by using Curtipot has been intensively tested for developing the model, and hence, the further verification is not necessary in here (the paragraph and the corresponding figures are suggested to be deleted. 9. Lines 251-254, these conclusions are not rigorous, because breakthrough of HONO can also occur for LOPAP. The authors are suggested to reveal the collection efficiencies’ range of HONO by Marga during actual measurements to support the statement of 200% HONO underestimation in the lowest pH in the abstract. 10. Lines 254-256, this sentence is meaningless, can be deleted. 11. Lines 268-274, these sentences can be concise, e.g., the sentence of “Therefore, a correlation . . .” can be deleted; the small fraction of NO<sub>2</sub> hydrolysis for HONO formation can be compared with the previous study in one sentence. 12. Lines 282-283, The explanation is not clear. 13. Lines 284-285, the competition (“complete SO<sub>2</sub> oxidation” in your text may mistyped) oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> and NO<sub>2</sub> in the atmosphere can be dated back in 1980s, is not original finding from Cheng et al. 14. Line 286, “a similar oxidation process” should be “the similar competition oxidation process”. 15. Lines 309-315, the equilibrium of HSO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>-</sup>, SO<sub>2</sub> in liquid should be very fast, the fast oxidation of HSO<sub>3</sub><sup>-</sup> by H<sub>2</sub>O<sub>2</sub> will be quickly compensated by a new equilibrium even under high pH values, e.g., the sulfate formation rate is almost independent of pH values through H<sub>2</sub>O<sub>2</sub> oxidation. Figure 6b illustrated may be in correct because the

shift of the equilibrium of sulfur species in the liquid is not considered. In addition, the liquid oxidation of SO<sub>2</sub> by O<sub>2</sub> also account for large fraction under basic condition, the nearly 100% sulfur oxidation by NO<sub>2</sub> at pH of 8 is not proper.

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