
Response to Editor

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1. Thank you for your consideration of the referee comments. Many of the comments have been addressed. However, please address the following comments prior to publication.

Reply: We appreciate your valuable comments and suggestions, which are very helpful for the further improvement of our manuscript.

2. Sect 2.2: Please indicate if the sampling tubes were covered (to prevent photochemistry of deposited species from causing interferences) and implications if not.

Reply: We appreciate your valuable suggestions. During the field campaign, the sampling tubes were not covered by opaque materials but were installed inside the iron tower to avoid direct sunlight. We have provided these details in the revised manuscript. [see P: 7; L: 152-153]

"All the sampling tubes were installed inside the iron tower to avoid direct sunlight."

3. Lines 217-219: Indicate where the zero air was added to perform the blank. Was the blank just of the instrument or of the instrument + the sampling lines?

Reply: We appreciate your valuable comments and suggestions. During the field campaign, blank measurements of the instrument were made by adding zero air to the inlet of the instrument without through the long tubes. We have conducted tests to investigate impacts of the long tubes on the blank measurements of the instrument. Background signals of the instrument made through the 400 m long tube for formic acid and isocyanic acid at a zero air flow rate of 13 SLPM have been provided in Figure S3 in SI. The difference between the average signals of formic acid measured with and without the 400 m long tube was only 5 ncps, accounting for a fraction of 1.4% in the sensitivity of formic acid (357.1 ncps/ppbv) and thus can be ignored. The average difference of the instrument background signal for isocyanic acid measured with and without the 400 m long tube was only 0.03 ncps, accounting for a very tiny fraction of 0.05% in the sensitivity of isocyanic acid (51.4 ncps/ppbv) and thus can also be ignored. These results indicate that the usage of the long tubes have minor effects on the blank measurements of the instrument for both formic acid and isocyanic acid. We have provided an additional discussion in the revised manuscript to tell the readers that the blank measurements of the instrument were made without through the long tubes. [see P: 9; L: 185-189]

"As shown in Figure S3, there was no significant difference between the background signals of the instrument made with and without the long tubes. Therefore, blank measurements of the instrument were made by adding zero air just to the inlet of the instrument without through the long tubes during the field campaign."

A detailed description of the test results is provided in SI. [see P: 3; L: 22-30]

"Figure S3 shows the background signals of the instrument made through the 400 m long tube for formic acid and isocyanic acid at a zero air flow rate of 13 SLPM. The difference between the average signals of formic acid with and without the 400 m long tube was only 5 ncps, accounting for a fraction of 1.4% in the sensitivity of formic acid (357.1 ncps/ppbv) and thus can be ignored. The average signal difference for isocyanic acid with and without 400 m long tube was only 0.03 ncps, accounting for a very tiny fraction of 0.05% in the sensitivity of isocyanic acid (51.4 ncps/ppbv) and thus can also be ignored. These results indicated that the usage of the long tubes had minor effects on the blank measurements of the instrument for both formic acid and isocyanic acid."

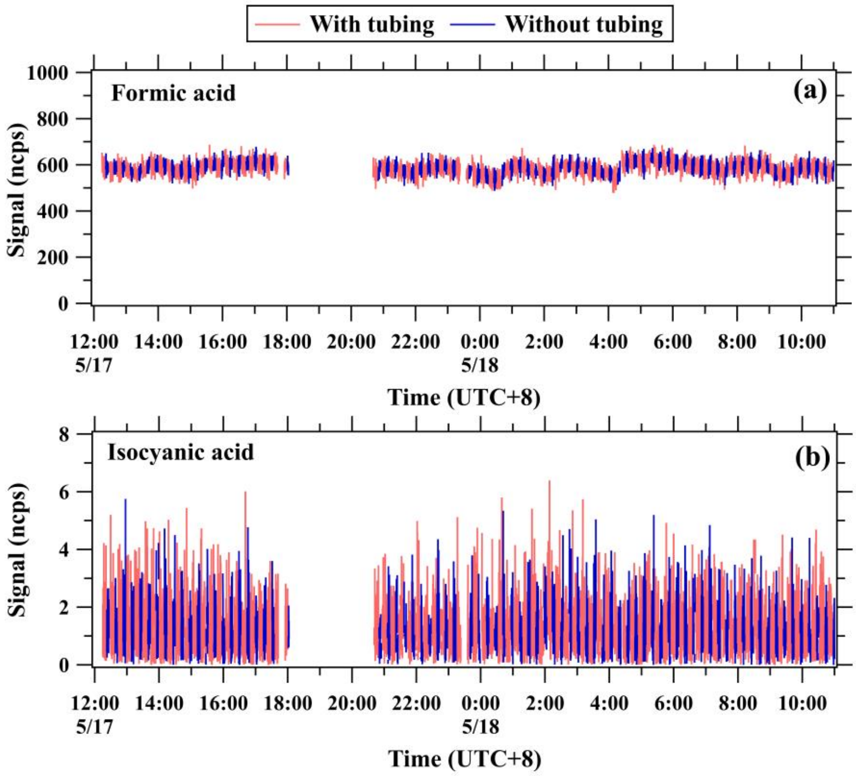

Figure S3. *Time series of (a) formic and (b) isocyanic acid blank signals measured with and without the 400 m long tube at a zero air flow rate of 13 SLPM.*

4. Referee 1 comment 10: Please expand on the discussion about how the delay time can be shorter than the residence time and incorporate this into the manuscript. While it may be discussed in a previous manuscript, it is central to this paper as well and should be included in at least a brief format.

Reply: We appreciate your valuable comments and suggestions. Residence time refers to the time required for the sample gas to pass through the tubes. As for the measured tubing delays of trace gases, they refer to the amounts of time required for the instruments to measure stable concentrations of targeted species in response to a change in species concentrations at the tubing inlet. Residence time is the same for all trace gases, depending on the length of the tube, the diameter of the tube, and the flow rate of the sample gas. However, the tubing delay of trace gases are different and depend on the flow rate, their respective saturated concentrations/Henry's constants, and molecular diffusion rates. We have provided related definitions and discussions in the revised manuscript. [see P: 13; L: 297-307]

"The delay time of formic acid mentioned here is different from the residence time of the gas through the long tubing. Residence time refers to the time required for the sample gas to pass through the tubes. As for the measured tubing delays of trace gases, they refer to the amounts of time required for the instruments to measure stable concentrations of targeted species in response to a change in species concentrations at the tubing inlet. The residence time is the same for all trace gases, depending on the length of the long tube, the inner diameter of the tube, and the flow rate of the sample gas. However, the tubing delay for each trace gas is different and depends on the flow rate, their respective saturated concentrations/Henry's constants, and molecular diffusion and diffusion rates. The difference between residence time and delay time is also discussed in detail in our previous work (Li et al., 2023)."

References:

(1) Li, X., Zhang, C., Liu, A., Yuan, B., Yang, H., Liu, C., Wang, S., Huangfu, Y., Qi, J., Liu, Z., He, X., Song, X., Chen, Y., Peng, Y., Zhang, X., Zheng, E., Yang, L., Yang, Q., Qin, G., Zhou, J., and Shao, M.: Emerging investigator series: Assessment of Long Tubing in Measuring Atmospheric Trace Gases: Applications on Tall Towers, Environmental Science: Atmospheres, 10.1039/d2ea00110a, 2023.

5. Line 287: What mixing ratios were used for the step-function change? Please include that in the text.

Reply: We appreciate your valuable comments and suggestions. The step-function change used in our study is 7.5-0 ppbv. During the test, a mixture of zero air and formic acid vapor with a formic acid concentration of 7.5 ppbv was first introduced into the 400 m long tube. After the stabilization of the measured formic acid signal, we stopped the supply of the formic acid vapor and only zero air was introduced into the instrument at the same flow rate. Then, the measured signals of formic acid through the long tube declined and we can obtain a depassivation curve of formic acid to calculate the tubing delay. We have rephrased this sentence in the revised manuscript to make it clearer. [see P: 11; L: 253-256]

"The depassivation curve of formic acid measured at the outlet end of the long tubing was used to calculate its tubing delay and was obtained by using a step-function change of the formic acid concentration from 7.5 ppbv to 0 ppbv at the tubing inlet (Pagonis et al., 2017; Deming et al., 2019)."

6. Line 352: Why is delta t defined here – it isn't used in equation 1.

Reply: Thank you for pointing out this mistake and we have adjusted the position of this sentence in the manuscript. [see P: 14; L: 333-335]

"

$$\Delta[X]_t = [X_{with}]_t - \frac{\sum_{t-\Delta t}^{t}[X_{with}]}{\Delta t} \qquad (2)$$

where Δt is the change in time relative to time t and was used to characterize the influential time of the memory effect."

7. Lines 386-388: I think this last sentence over simplifies the formic acid discussion and may cause confusion to readers. I recommend clarifying that formic acid does suffer from memory effects that need to be considered when interpreting the measurements.

Reply: We appreciate your valuable comments and suggestions. The test results confirmed that the measurements of formic acid and isocyanic acid through long tubes can be used to characterize their vertical and temporal variability. However, a further correction of the formic acid measurements made through the long tubes must be performed if they were used to accurately calculate the kinetic parameters of chemical reactions regarding the formation and removal of formic acid at different heights. We have rewritten this sentence in the manuscript to make it clearer. [see P: 15-16; L: 375-380]

"The test results confirmed that the measurements of formic acid and isocyanic acid through long tubes can be used to characterize their vertical and temporal variability. However, a further correction of the formic acid measurements made through the long tubes must be performed if they were used to accurately calculate the kinetic parameters of chemical reactions regarding the formation and removal of

formic acid at different heights.”

8. Referee 1 comment 14/Referee 2 comment 4: Please include the information about the 200 m tubing test in the manuscript to explain why the 200 m appears to be an outlier in Fig. 3.

Reply: We appreciate your valuable comments and suggestions. During the test of the 200 m tubing, meteorological conditions significantly changed with lower temperatures and stronger winds in comparison to the days on which the tests of the other lengths of tubes were performed. As shown in Figure S5, the concentrations of formic acid and isocyanic acid were evidently enhanced and significantly varied during the 400 m tubing test. In contrast, ambient concentrations of formic and isocyanic acid were relatively low and slightly varied, resulting in the exceedingly large or low values of k and R^2 between the concentrations of formic acid measured with and without the 200 m long tubing. However, according to the results of the test, the average concentration difference of formic and isocyanic acid measured with and without the 200 m tubing agreed well within 4%, suggesting that the 200 m long tube has minor effects on the measurements of formic and isocyanic acid. We have provided these results and discussions in the revised manuscript. [see P: 15; L: 351-362]

“During the test of the 200 m tubing, meteorological conditions significantly changed with lower temperatures and stronger winds in comparison to the days on which the tests of the other lengths of tubes were performed. As shown in Figure S5, the concentrations of formic acid and isocyanic acid were evidently enhanced and significantly varied during the 400 m tubing test. In contrast, ambient concentrations of formic and isocyanic acid were relatively low and slightly varied, resulting in the exceedingly large or low values of k *and* R^2 *between the concentrations of formic acid measured with and without the 200 m long tubing. However, according to the results of the test, the average concentration difference of formic and isocyanic acid measured with and without the 200 m tubing agreed well within 4%, suggesting that the 200 m long tube has minor effects on the measurements of formic and isocyanic acid.”*

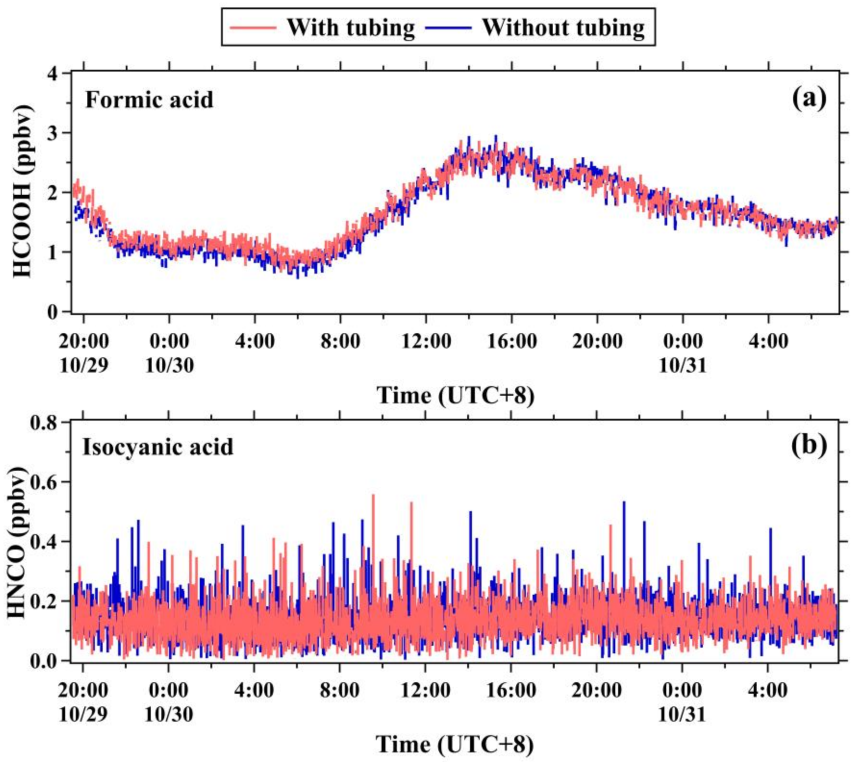

Figure S5. *Time series of (a) formic and (b) isocyanic acid concentrations measured with and without the 200 m long tube.*

9. How was the PBL height measured?

Reply: We appreciate your valuable comment. The planetary boundary layer height (PBLH) is the reanalysis data obtained from the website of the NOAA Air Resources Laboratory (https://ready.arl.noaa.gov/READYamet.php). We have provided an additional description on the source of the PBLH data in the revised manuscript. [see P: 10; L: 220-224]

"The planetary boundary layer height (PBLH) data was obtained from the web portal of the Real-time Environmental Applications and Display sYstem (READY) of the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (https://ready.arl.noaa.gov/READYamet.php)."

10. Lines 521-524: The CICs consider the residual layer which will not have depositional loss occurring. The ground-level measurements will have stronger depositional loss at night. I'm not sure how looking at ground-level measurements is thus overestimating removal. In fact, it seems like considering CICs will underestimate the removal. Please clarify.

Reply: We appreciate your valuable comments and agree with your opinion that ground-level measurements are more affected by depositional losses, while such losses in the residual layer are minor. By using CICs, we want to highlight the change in the total budget of formic acid within the entire boundary layer. The residual layer is formed due to the shrimp of the boundary layer and thus can be considered part of the boundary layer. Due to the absence of depositional loss, large amounts of formic acid retained in the residual layer during the night can entrained into the boundary layerduring the daytime. If the removal rates of formic acid from ground-level measurements are used to reflect those at high altitudes (e.g., in the residual layer), the removal of formic acid in the entire atmospheric boundary layer will be overestimated. We have rewritten this sentence in the manuscript to make it clearer. [see P: 20; L: 508-514]

"The ground-level measurements were more affected by depositional losses, while such depositional losses in the residual layer were nearly absent. However, the chemical species retained in the residual layer were closely related to their budgets in the daytime boundary layer. If the removal rates of formic acid from ground-level measurements were used to characterize those at high altitudes (e.g., in the residual layer), the removal of formic acid in the entire boundary layer would be overestimated."