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Measurement report: Enhanced photochemical formation of formic and isocyanic acids in urban regions aloft – insights from tower-based online gradient measurements

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Vertical observation system during the campaign

Table S1. Flow rates and residence times of the different lengths of tubes during the field campaign.

Length of tubing (m)	Altitude (m)	Flow rate (SLPM)	Calculated residence time (s)
~4	5	20.4	0.8
100	47	17.7	24.0
150	102	17.8	35.8
250	200	15.5	68.6
400	320	13.6	125.0

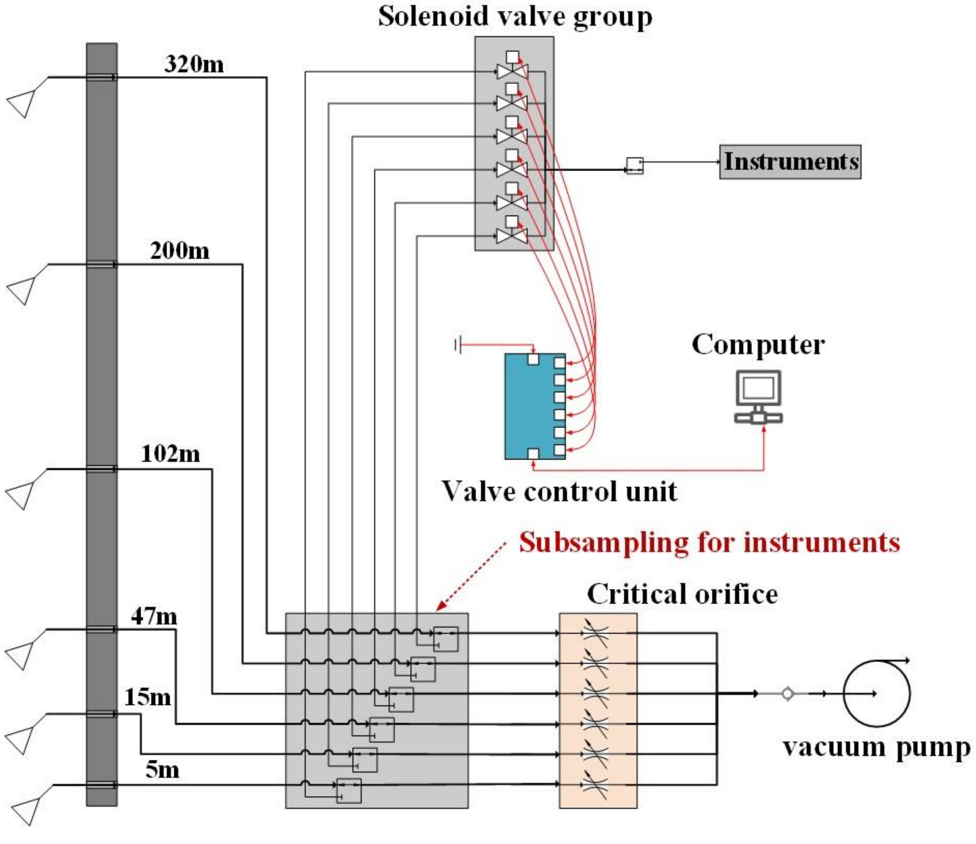

Figure S1. A simple schematic illustration of the vertical observation system on the Beijing and locations of the five sampling inlets for measuring atmospheric gaseous species.

Tubing test

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.

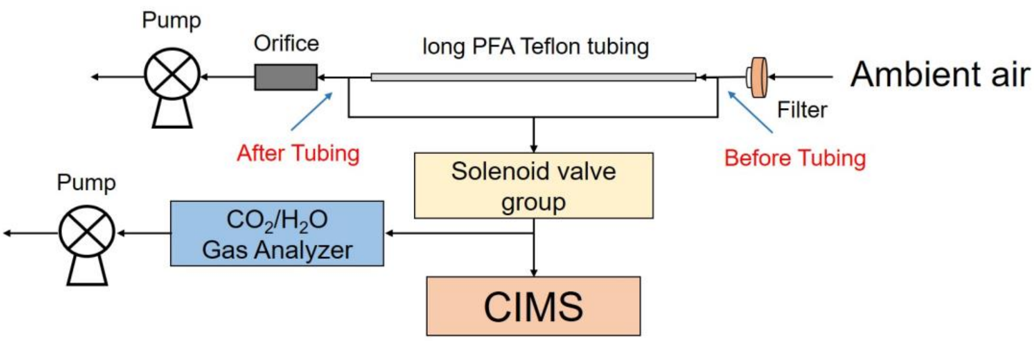

Figure S2. Schematic illustration of the PFA Teflon tubing tests for formic and isocyanic acids.

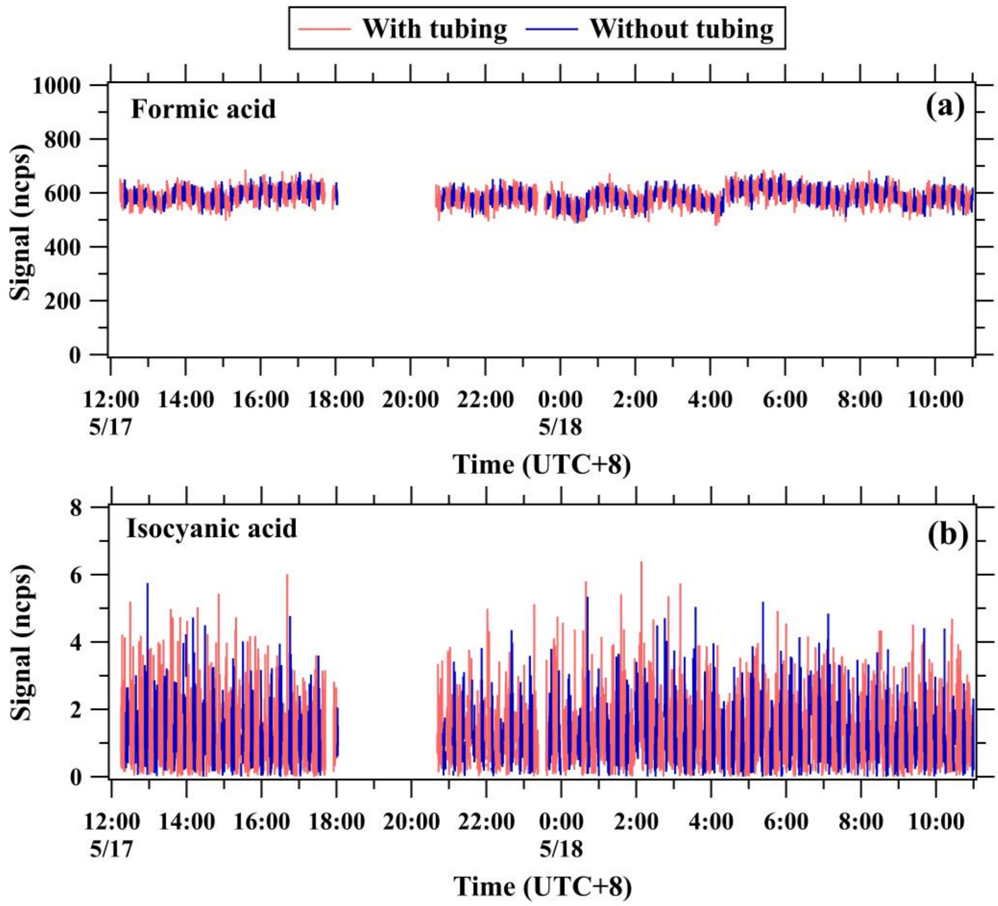

Figure S3. Time series of (a) formic and (b) isocyanic acid blank signals measured with and without the 400 m long tube at a zero air flow rate of 13 SLPM.

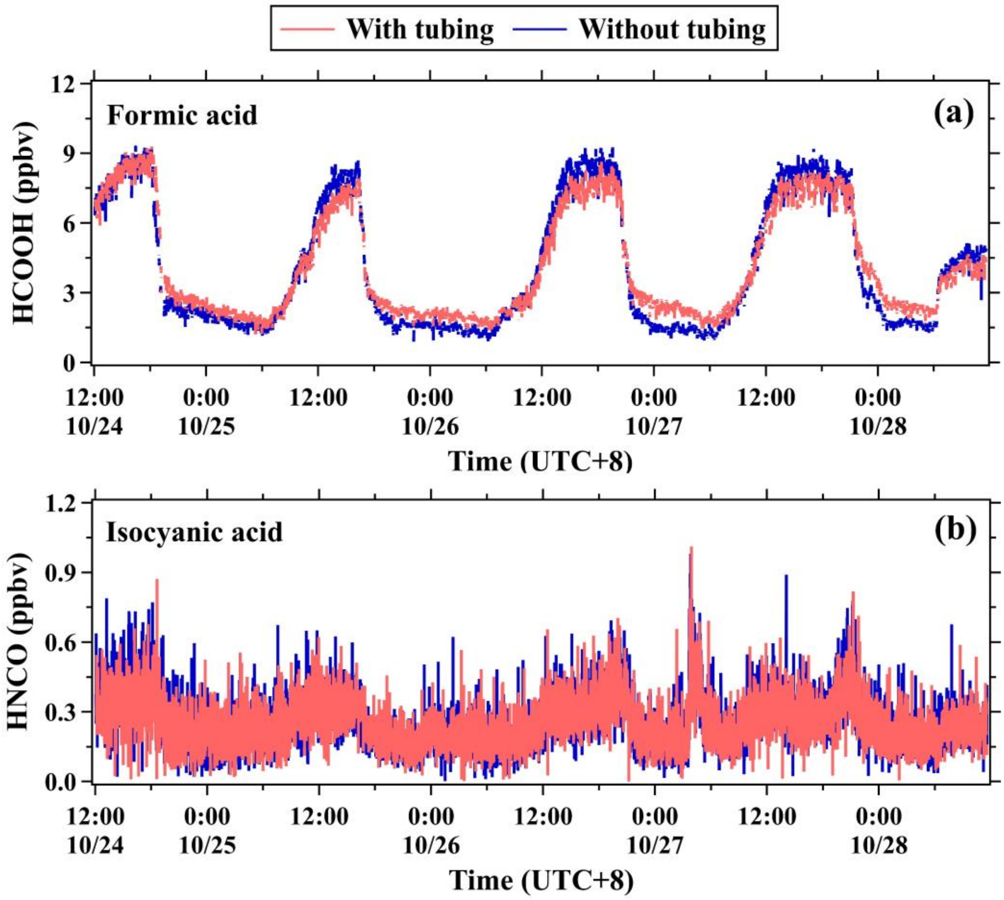

Figure S4. Time series of (a) formic and (b) isocyanic acid concentrations measured with and without the 400 m long tube.

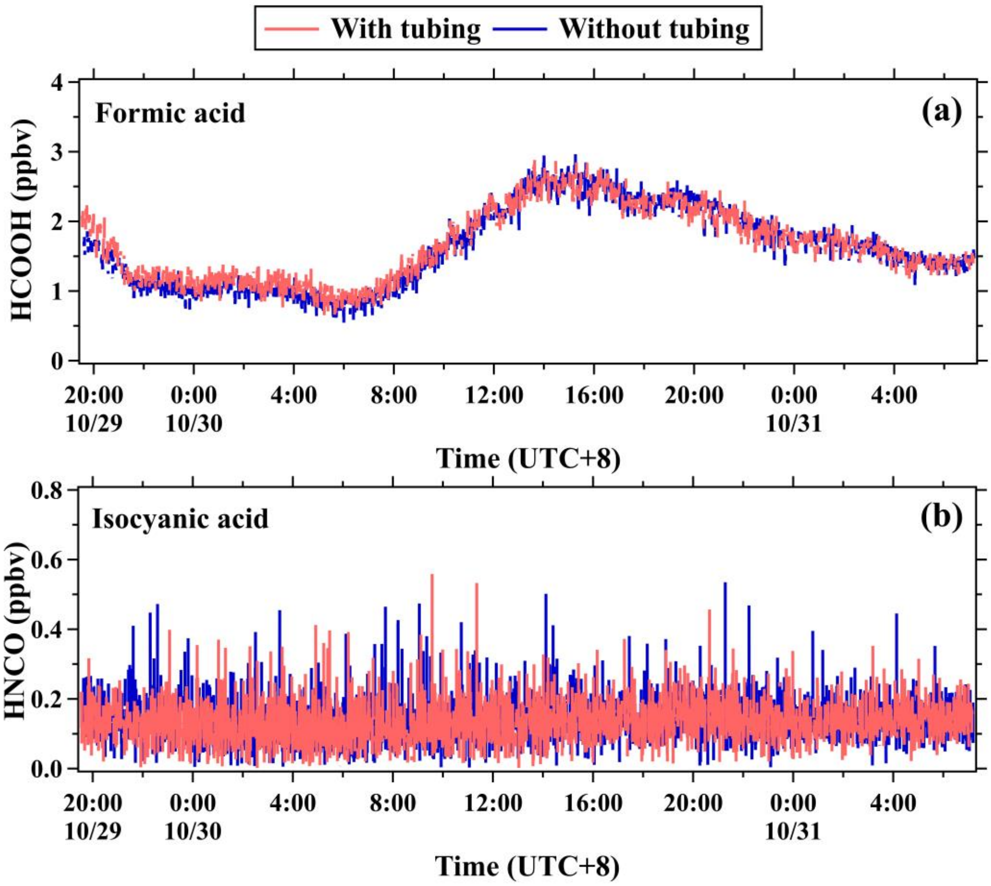

Figure S5. Time series of (a) formic and (b) isocyanic acid concentrations measured with and without the 200 m long tube.

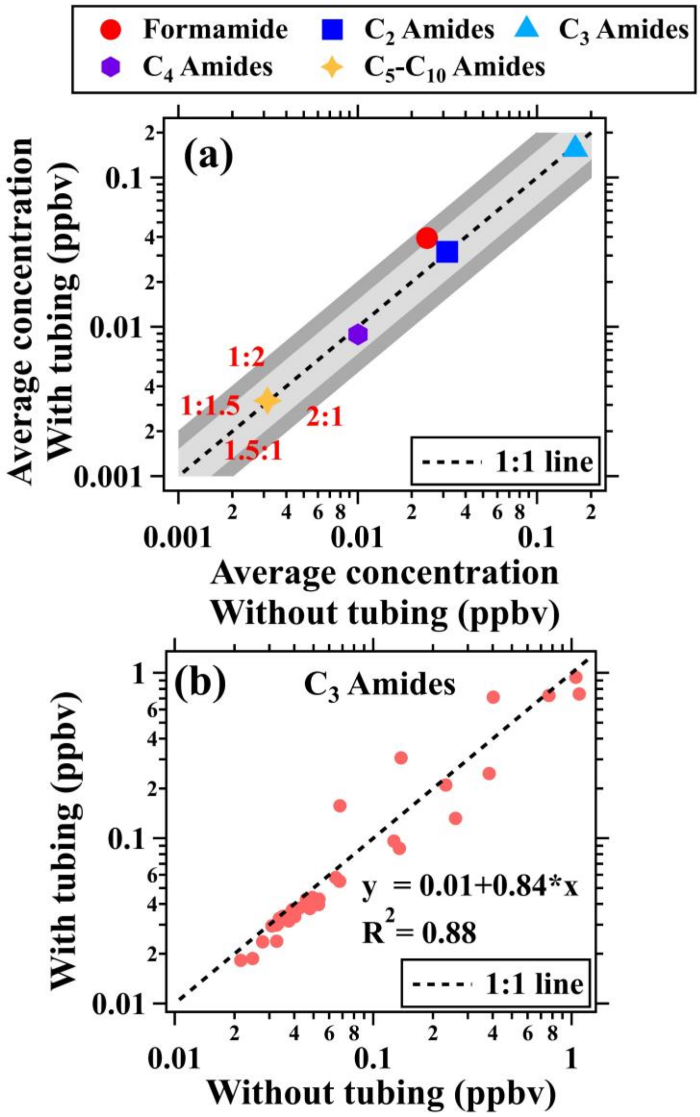

Figure S6. Assessment of the 400 m tubing in measuring amides in ambient air. (a) Average concentration ratio of amides with and without long tubing. (b) Scatterplots of mixing ratios of C_3 amides measured with the 400 m long tube versus those measured without the long tube.

Determination of the cumulative influence time Δt

To determine the cumulative influence time Δt of formic and isocyanic acids when made through the 400 m long tube, 0 to 24 h were substituted into the value of Δt sequentially at intervals of 1 h. Correlation coefficients (R^2) between $\delta[X]_t$ and $\Delta[X]_t$ for the measurements of formic and isocyanic acids were calculated and shown in Figure S3. The correlation coefficients between $\delta[X]_t$ and $\Delta[X]_t$ for formic acid showed a unimodal pattern with the increase of Δt and reached the peak at Δt=14 h (R^2=0.89). This strong correlation proves that our speculation about the influence of the memory effect of long tubing on formic acid measurements is correct. In contrast to formic acid, poor correlations (R^2<0.01) between $\delta[X]_t$ and $\Delta[X]_t$ were observed for isocyanic acid. Therefore, the measurements of isocyanic acid made through the 400 m long tubing were insignificantly affected by interactions between isocyanic acid molecules and tubing inner walls.

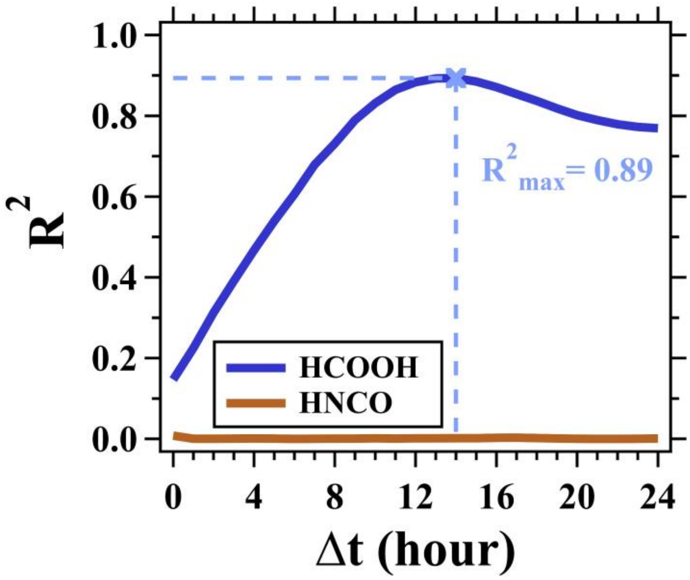

Figure S7. The change in correlation coefficients (R^2) between $\delta[X]_t$ and $\Delta[X]_t$ for the measurements of formic and isocyanic acids as a function of Δt.

Calculation of column-integrated concentrations (CICs)

Column-integrated concentrations (CICs) were calculated to characterize the abundance and diurnal variability of formic and isocyanic acids in the whole boundary layer. Due to the diurnal changes in heights of the planetary boundary layer, the high concentrations of formic and isocyanic acids in the nocturnal residual layer have important contributions to their budgets in the boundary layer. Therefore, CIC is defined as the total number of molecules from the surface to the top of the atmospheric boundary layer (L_{amex}) over a unit area (cm^{-2}). Eq. (S1) provides the theoretical calculation formula of CIC:

$$CIC(i)_t = \int_0^{L_{max}} [i]_h \, dh \times \frac{N_A}{V_{molar}(h)} \qquad \text{(S1)}$$

where $CIC(i)_t$ represents the CIC (*unit: molecule* cm^{-2}) of the species *i* (namely formic and isocyanic acids) at time *t*. $[i]_h$ represents the mixing ratio of species *i* (*unit:* 10^{-9} *mol* mol^{-1}) at an altitude *h* (*unit: cm*). L_{max} is the maximum height of the planetary boundary layer (PBLH) at time *t*. On any given day, L_{max} is defined as the maximum PBLH the day before if the PBLH has not reached its maximum on that day. Otherwise, L_{max} is defined as the maximum PBLH on that day, as shown in Figure S4. N_A is the Avogadro constant (6.02×10^{23} *molecule* mol^{-1}). V_{molax} (*h*) is the molar volume of gas at the height of h and can be calculated based on the measurements of atmospheric temperature (*unit: K*) and pressure (unit: hPa) using the ideal gas law.

Due to the limited height of the tower, the concentrations of formic and isocyanic acids between the maximum measurement height (320 m) and the top of the boundary layer were assumed to be equal to those measured at 320 m. It should be noted that this assumption may underestimate the CICs of formic and isocyanic acids due to their positive vertical gradients. The diurnal variation patterns of CICs for formic and isocyanic acids were not significantly changed by this assumption due to their larger vertical gradients in daytime than in nighttime. The linear interpolation method was used to estimate concentrations of formic and isocyanic acids between two measurement heights.

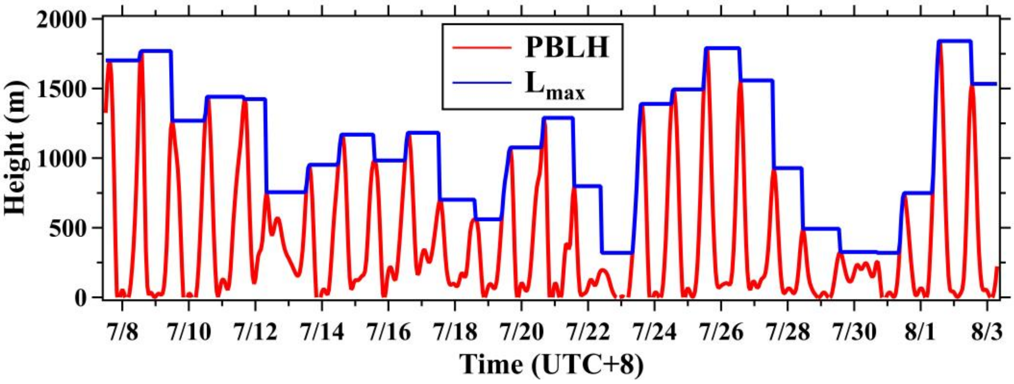

Figure S8. Time series of the PBLH and L_{max} during the field campaign.