Supporting Information for “Measurement report: Enhanced photochemical formation of formic and isocyanic acids in urban region aloft: insights from tower-based online gradient measurements”

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**Tubing test**

**Figure S1.** Schematic illustration of the PFA Teflon tubing tests for formic and isocyanic acids.

**Figure S2.** Time series of (a) formic and (b) isocyanic acids concentrations measured with and without the 400 m long tube.
Determination of the cumulative influence time $\Delta t$

To determine the cumulative influence time $\Delta t$ of formic and isocyanic acids when made through the 400 m long tube, 0 to 24 h were substituted into the value of $\Delta t$ 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 $\Delta t$ and reached the peak at $\Delta t=14$ 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 S3. 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 $\Delta t$. 
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 \((L_{\text{max}})\) over a unit area \((\text{cm}^2)\). Eq. (S1) provides the theoretical calculation formula of CIC:

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

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