

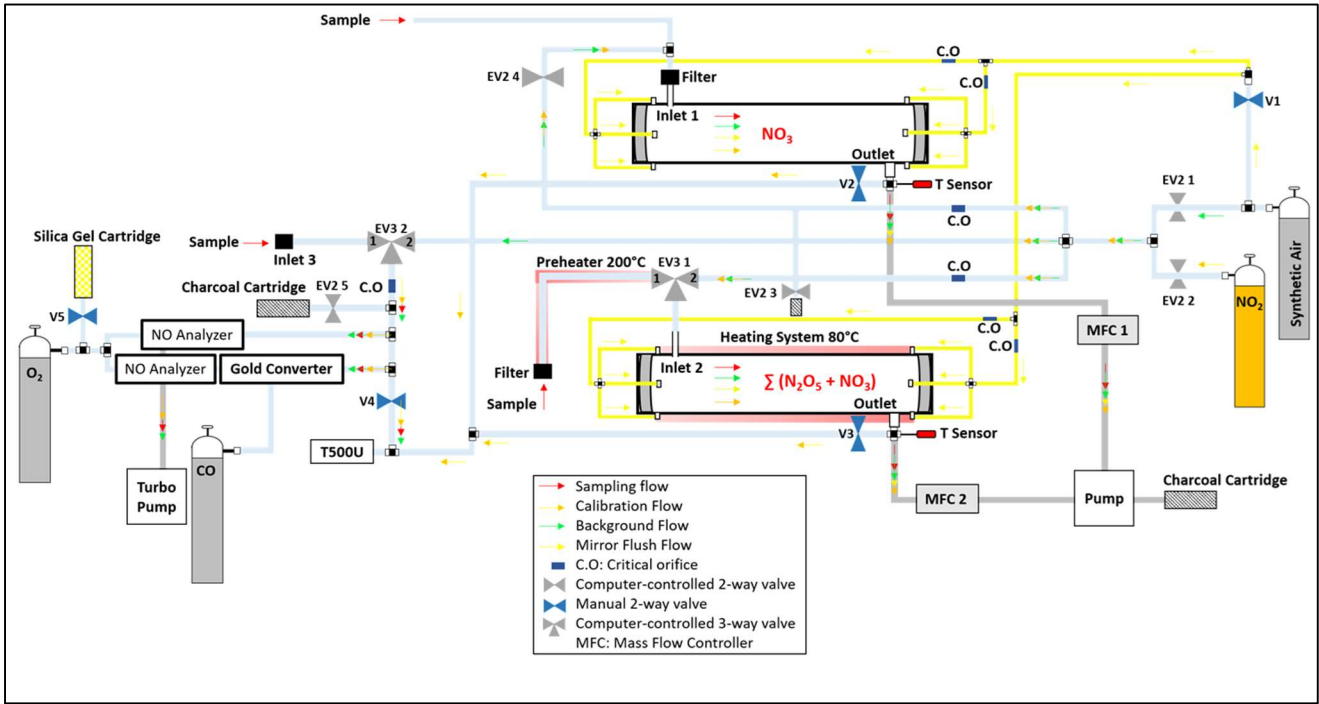


Figure S1. Detailed schematic diagram of the NOyBOx instrument and its flow system.

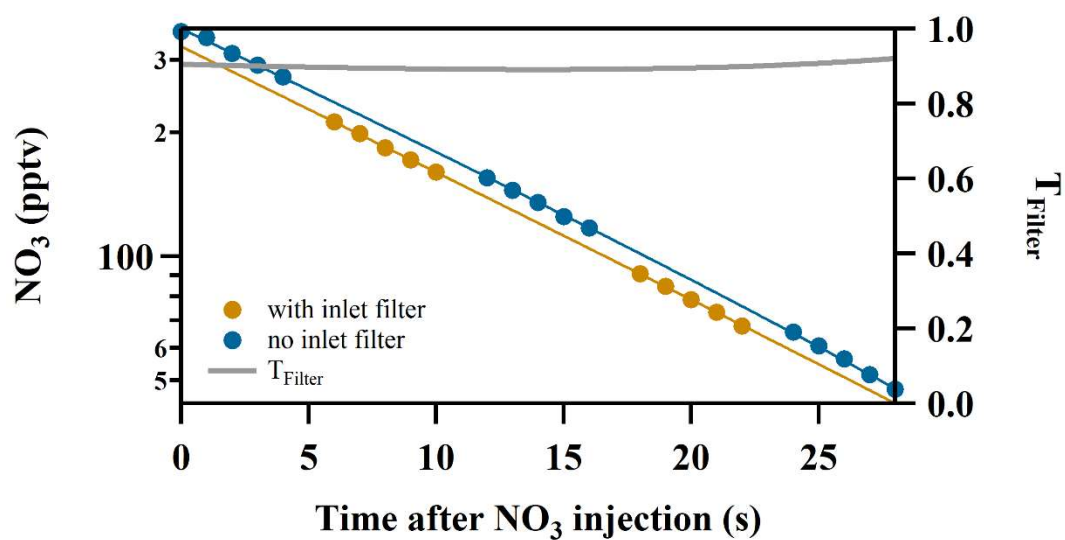
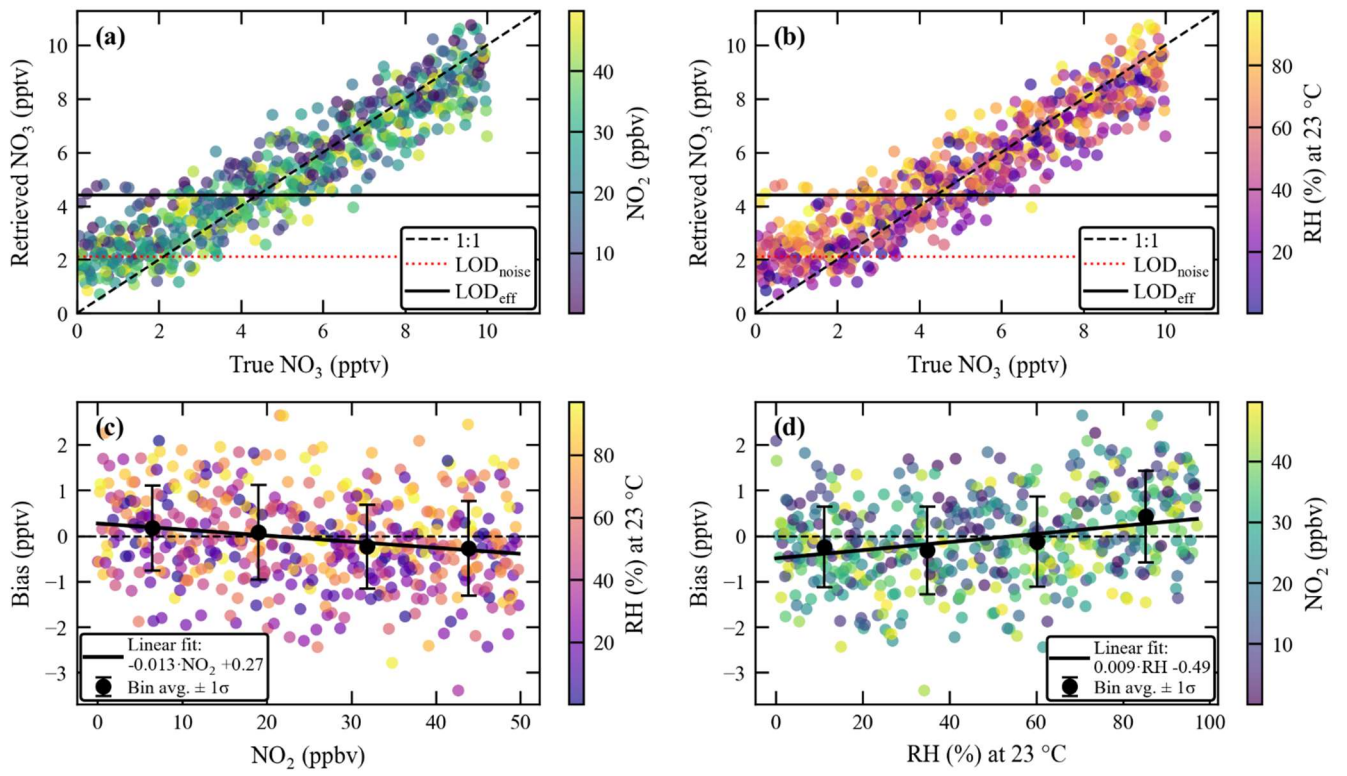
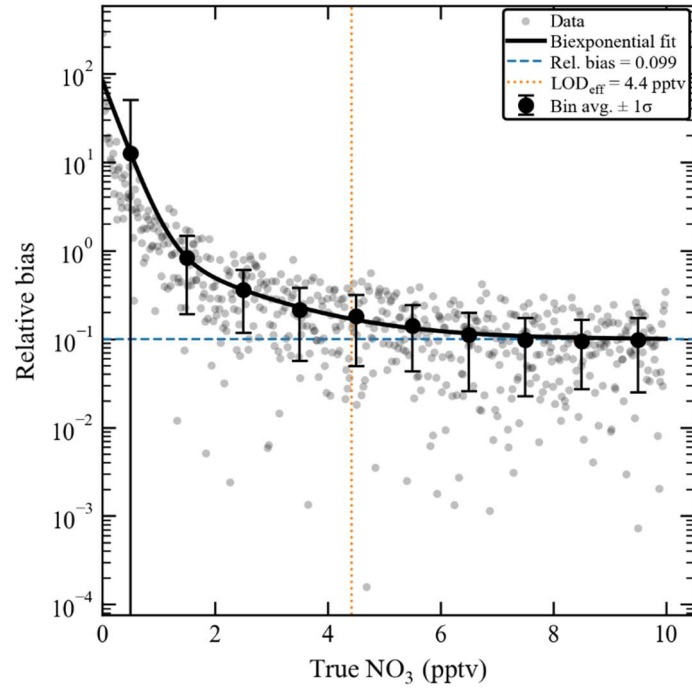


Figure S2. Decay of NO_3 as a function of time after NO_3 injection into the CESAM chamber, sampled with (orange) and without (blue) the inlet filter installed. Solid lines represent exponential fits to the respective decay curves. The filter transmission (T_{Filter} , grey, right axis), calculated as the ratio of the two fitted decays, remained close to 0.9 throughout the measurement.



20 **Figure S3.** Retrieval performance of the NO_3 fitting routine as a function of interfering NO_2 and water vapor, based on Monte Carlo
simulations of synthetic spectra for the N_2O_5 channel (10 noise realisation points average, 600 LHS points): (a, b) Retrieved vs. true NO_3
mixing ratio, with points colored by (a) true NO_2 (ppbv) and (b) relative humidity (RH, % at 23°C). The dashed line indicates the 1:1
relationship; the dotted red line marks $\text{LOD}_{\text{noise}}$ derived from the Allan deviation, and the solid black line marks the effective detection
limit LOD_{eff} , which additionally incorporates the standard deviation (2σ) of the retrieval bias across all simulated spectra. (c, d) Retrieval
25 bias (retrieved – true NO_3) for points $\text{NO}_3 > \text{LOD}_{\text{noise}}$ plotted against (c) NO_2 and (d) RH, colored by the complementary variable in each
case. Black circles show bin-averaged values ($\pm 1\sigma$). Black lines show weighted linear fits to the bin-averaged points.



30 **Figure S4.** Relative bias in retrieved NO_3 ($|\text{retrieved} - \text{true}| / \text{true}$) versus true NO_3 concentration from Monte Carlo simulations for the N_2O_5 channel. Gray points: individual retrievals; black circles: quantile-binned means $\pm 1\sigma$. Solid line: biexponential fit with parameters (a_1, a_2, b_1, b_2, c), relative bias = $a_1 \times \exp(-b_1 \times \text{NO}_3) + a_2 \times \exp(-b_2 \times \text{NO}_3) + c$, capturing the noise-dominated divergence at low NO_3 and the systematic interference floor ($c = 0.099$, blue dashed line) at higher NO_3 . Orange dotted line: effective LOD.