Supporting Information for Evaluating N_2O Analyzers for Urban Monitoring: Evidence for Underestimated Emissions

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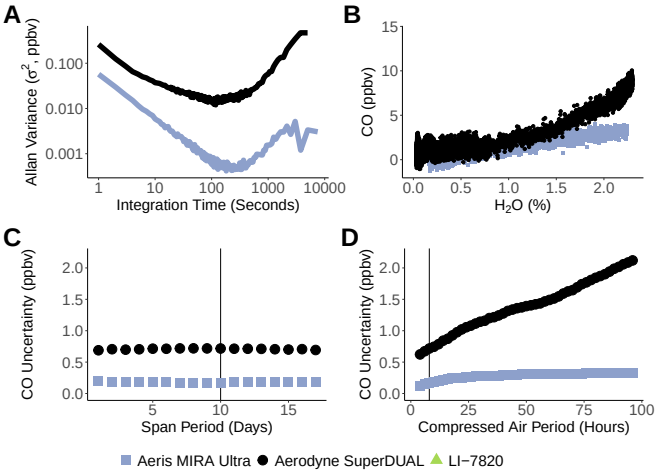

Figure S1. Characterization of the CO measurements of the Aerodyne QCLS (black circles) and Aeris MIRA Ultra (blue squares). The LI-7820 does not measure CO so does not appear. Panels are the same as in Figure 1.

S1. Characterization of CO Analyzers

We also analyzed the same tests we ran for N_2O to characterize the CO measurements on the Aerodyne QCLS and Aeris MIRA Ultra. For precision, the Aeris MIRA Ultra substantially outperforms the Aerodyne QCLS, with superior 1-second precision and less impact of analyzer drift (Figure S4A). This is consistent with the guidance from Aerodyne to calibrate their analyzer up to once an hour for baseline shifts.

For the humidity dependence, the Aerodyne QCLS exhibits a quadratic dependence, with reported CO changing by around 5 ppbv at 2% H_2O. The Aeris MIRA Ultra had a linear dependence, with an estimated humidity dependence of 1.78 $\frac{ppbv}{\%\ H_2O}$. The corrections for both analyzers were consistent and simple to correct, though the Aerodyne QCLS sensitivity also changed after we re-did the etalon fit (Figure S4B).

In the tests of the analyzer stability, the Aeris MIRA Ultra consistently outperformed the Aerodyne QCLS (Figure S4C and D). The frequent intercept adjustments are necessary for the CO measurements, as we observed unpredictable drift over time periods shorter than a day.

S2. Choice of Background

Previous work for methane and CO_2 has found the best agreement between the 5th percentile at urban sites and upwind towers. Therefore, the 5th percentile is the most common choice of background mole fraction in the absence of a dedicated upwind tower. However, urban areas account for a lower fraction of global N_2O emissions and this may not apply equivalently to N_2O. Without a dedicated background tower, we instead processed our data using several possible percentiles for the background. We found the best agreement across sites and years using the 30th percentile for the background and therefore used this value in the main text (Figure S2).

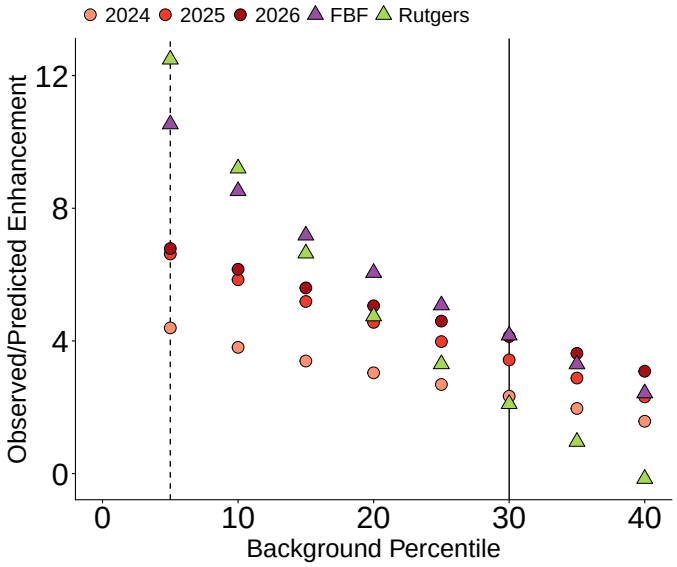

Figure S2. Ratio of observed N_2O enhancements for the three years of measurements at CUNY and the two other sites to predicted enhancements from the convolution of HRRR-STILT footprints with EDGARv2024. The agreement across years and sites is best using the 30^{th} percentile background (solid line). The dashed line at the 5^{th} percentile represents a typical percentile in the literature.

S3. NAM3 Meteorology

We also tested the North American Mesoscale 3-km (NAM3) meteorology to check the dependence of our conclusions on the chosen meteorology. NAM3 footprints were only available starting in July of 2025 and therefore not available for the Rutgers deployment. On average, using the NAM3 meteorology results in slightly lower predicted enhancements than using HRRR for the CUNY site. At FBF the mean ratio of observed enhancements to predicted was 3.07, compared to 4.17 using HRRR, () while at CUNY it went down to 2.70 () from 3.23 using HRRR. The average across the two sites with NAM3-driven footprints was 2.81.

S4. Stability of Compressed Air Measurements

We used the stability of the compressed air measurements as a proxy for the calibration-related uncertainty in Figure 1. The LI-7820 N_2O measurement shows a cyclical pattern with a period of 2-3 days that can be easily removed with a frequent intercept calibration. The Aerodyne QCLS CO measurement has a similar but more irregular pattern, consistent with the manufacturer's suggestion to calibrate the intercept hourly. The Aeris MIRA Ultra showed drift over time in both the N_2O and CO measurements that can be removed with daily calibration.

S5. Cell Size Impact on Mobile Measurements

During the TEEMS measurement campaign, the LI-7820 and Aeris MIRA Ultra sampled from the same inlet line. However, the LI-7820 has a smaller cell (6.41 cm^3) than the Aeris (60 cm^3) but a similar flow rate (250 sccm for the LI-7820 and 300 sccm for the Aeris MIRA Ultra). Therefore, the LI-7820 has a faster response time and reports sharper plumes than the Aeris MIRA Ultra. We consistently observed higher peaks for plumes with the LI-7820 and longer durations for the Aeris MIRA

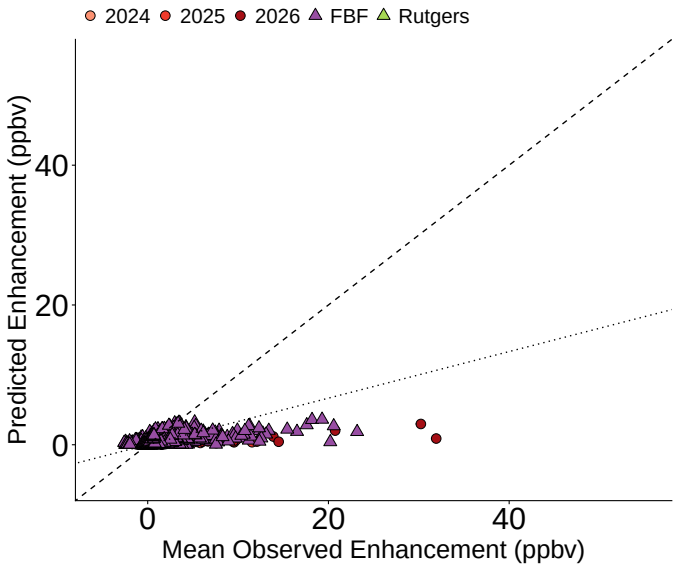

Figure S3. Comparison of observed and predicted N_2O enhancements using EDGARv2024 convolved with NAM3-STILT. The 1:1 (dashed) and 1:3 (dotted) lines are included for reference. This figure is the same as Figure 4B except for the meteorology driving STILT.

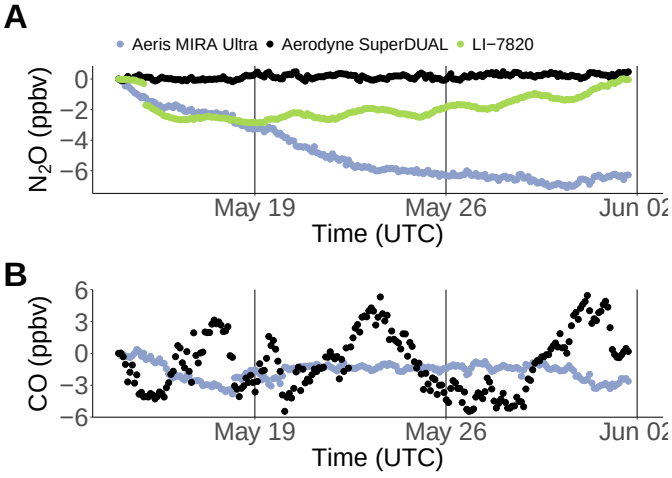

Figure S4. Time series of the deviations in the observed mole fractions of the compressed air tank, expressed as the value of the first observation minus every other observation. N_2O is shown in panel A) and CO is show in panel B). Each week since the beginning of the deployment is marker with a vertical line. The LI-7820 (green) shows a jump in the N_2O values on May 14.

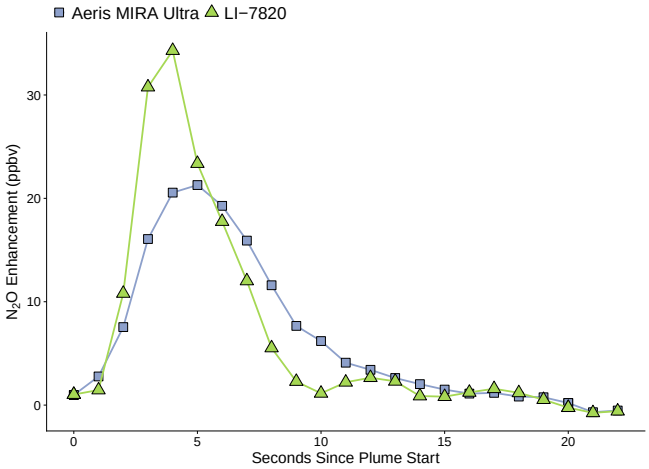

Figure S5. Comparison of plume width for the TEEMS mobile measurements. The area under the curve for the LI-7820 was 153 ppbv·sec and 148 ppbv·sec for the Aeris MIRA Ultra.

Ultra (Figure S5). However, the area under the curve typically agrees within 11% between the analyzers. Previous work with methane has emphasized the importance of using peak area rather than maximum enhancement for plume detection in mobile measurements for all gases Mønster et al. (2014); Albertson et al. (2016).

S6. Wind Direction Dependence of N_2O Enhancements

1-minute resolution winds were measured throughout the deployment of the Aerodyne SuperDUAL at CUNY on a Vaisala Weather Transmitter WXT530. We observed the largest peaks in the N_2O mole fraction at the CUNY site when winds came from the southeast in the direction of Wards Island WWTP. This peak was much sharper on the north end of the plume (100-140 degrees) than on the south end (150-230 degrees) due to a dome near the sampling point that can create eddies when winds came from the 150-230 degrees wind direction. An elevated highway and bridge over Wards Island may also cause the plume to disperse. We also observed significantly more variability in enhancements from the direction of Wards Island, with 1 Hz enhancements sometimes exceeding 100 ppbv.

S7. Supporting Information from Dhall et al.

The information included in this section is taken from a manuscript in submission and under review at ACS ES&T Air by Raghav Dhall et al. entitled "Transportation Related Sources of Nitrous Oxide" and included here for reviewers. If the Dhall paper is published before the final submission of this paper, a citation to it will be added in place of this section in the supporting information.

S7.1 Deployment Details

"*We deployed an Aeris MIRA Ultra $N_2O/CO/H_2O$, a LI-COR LI-7810 ($CO_2/CH_4/H_2O$) and a GPS receiver in the back of a vehicle (the NYAAQ Mobile Laboratory). Ambient air was sampled from an inlet mounted on top of the vehicle, 1.8 m above the ground. Previous testing had shown limited changes in instrument response (span) for each analyzer between power cycles. Calibrations before the first and after the last drive, for each sampling period, were consistent for each gas and the mean*

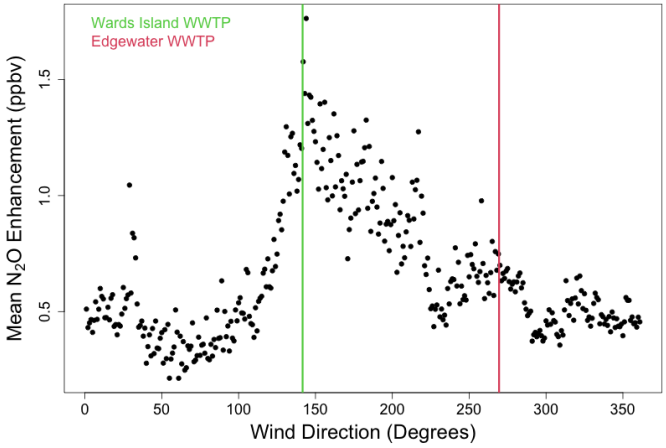

Figure S6. Mean N_2O enhancements observed at the CUNY tower binned as a function of wind direction. The wind directions associated the Wards Island WWTP and Edgewater WWTP are marked with green and red lines, respectively.

calibration factor was applied. Calibrations were performed using the NOAA-2006A standard for N_2O, the WMO-X2014A standard for CO, the WMO-X2019 standard for CO_2 and the WMO-X2004A standard for CH_4. The data Quality Control (QC) procedure ensured that the environmental parameters of all instruments and laser fit parameters were within optimal operating conditions. The water vapor dependence of each instrument was previously characterized (using methods described in Commane et al. (2023)) and applied to the data.

Deployments were conducted over five consecutive days in Winter (January 27-31 2025) and Summer (June 2-6 2025). We sampled the Upper East Side and East Harlem neighborhoods in Manhattan, NYC ($72^{nd} - 110^{th}$ Street, $1^{st} - 5^{th}$ Avenue). Driving the route took 4-5 hours, with an additional hour for setup. There were no wastewater treatment plants located within the deployment area, however Wards Island Wastewater Treatment Plant is located 1.5-2 miles east of the deployment area. The average speed during plume sampling was 9.25 mph. The drives were conducted in Manhattan during the day, when bus activity was high and heavy-duty trucks were relatively uncommon within the neighborhoods sampled. The sampled plumes were visually and temporally associated with identifiable MTA buses, and no other heavy-duty vehicles were consistently present during sampling."

7.2 Determining N_2O Emissions from Buses

"*Enhancements for each trace gas (ΔX) were calculated as the difference between the observed trace gas mixing ratio and the background: $\Delta X = \mathrm{Observed\ X} - \mathrm{Background\ X}$. The background was defined as the median of a 5-minute centered running window. Enhancements were clustered together to form plumes if they occurred within 1 second of each other. This interval corresponds to the instrument sampling frequency. In total, we observed 729 plumes with N_2O enhancements greater than 5 ppbv, 627 of which had CO enhancements greater than 50 ppbv. These thresholds were selected to reduce the influence of instrument uncertainty and include only larger enhancements. As the source of some of these N_2O plumes could not be confidently identified, and to ensure we isolated traffic related emissions, we based our analysis on CO plumes. We identified 2,444 plumes of CO with a peak enhancement above 50 ppbv, and found that 548 of these plumes contained N_2O above 5 ppbv. Around 160 of these plumes with N_2O showed strong correlations with CO ($R^2_{\mathrm{N_2O/CO}} \geq 0.9$) and around 200 of them showed strong correlations with CO_2 ($R^2_{\mathrm{N_2O/CO_2}} \geq 0.6$).*

After the plumes were extracted, we calculated the 5th percentile baseline for each trace gas enhancement for each 20 s plume. Defining a separate baseline was especially important for localized changes in the background of CO and CO_2 as there were other large sources of both gases unrelated to buses that were not captured in the enhancements calculated from

the 5 minute background. For each plume, we calculated the N_2O/CO_2 emission factors and CO integrated enhancements and matched them with identified buses where possible. We then categorized the N_2O emissions by the type of buses.

Using a carbon mass balance approach described in previous plume-based emission factor estimation studies (Wren et al., 2018; Chu et al., 2024), an emission factor can be estimated in units of mg N_2O / km. We assume a carbon mass fraction in diesel fuel of 0.87 (as in Wren et al. (2018)) and a mileage of 3.7 miles per gallon for diesel buses and 4.5 miles per gallon for hybrid electric buses (obtained from a 2022 MTA report (Ward, 2022)) for this calculation. Our study sampled buses under real-world driving conditions without cold starts, but we observed N_2O emissions within the range of those reported in earlier studies.

Overall, we sampled bus types that represent 87% of the buses across the MTA fleet (Ward, 2022). We multiplied the annual CO_2 emissions estimated for each bus type (Ward, 2022) with the 50% Confidence Interval (C.I.) of the N_2O/CO_2 emission factors to calculate the corresponding N_2O flux for each bus type. We then calculated the median annual N_2O flux from the MTA bus fleet as 31 (± 14) tonnes-N_2O yr^{-1}.

The EDGAR N_2O inventory estimated 212 tonnes-N_2O emissions from on-road vehicle transportation from NYC for 2023 (Crippa et al., 2024). Our results suggest that N_2O emissions from the less than 6000 MTA buses alone could contribute $9-21\%$ of the on-road N_2O emissions."

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