Characterizing the Aging of Alphasense NO_2 Sensors in Long-term Field Deployments

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1. Information of reference sites

The ACHD Lawrenceville and the CMU campus site are two collocation sites where reference instruments can provide accurate NO_2 concentrations. RAMP monitors were brought back to these two locations periodically for evaluating the data quality of NO_2 sensors. The minimum, mean, and maximum NO_2 concentrations in 2019 at the ACHD Lawrenceville are 0, 11.8, and 100.9 ppb, respectively. The minimum, mean, and maximum NO_2 concentrations in the 2017 collocation campaign at the CMU campus site from May to November were 0, 6.2, and 32.2ppb, respectively.

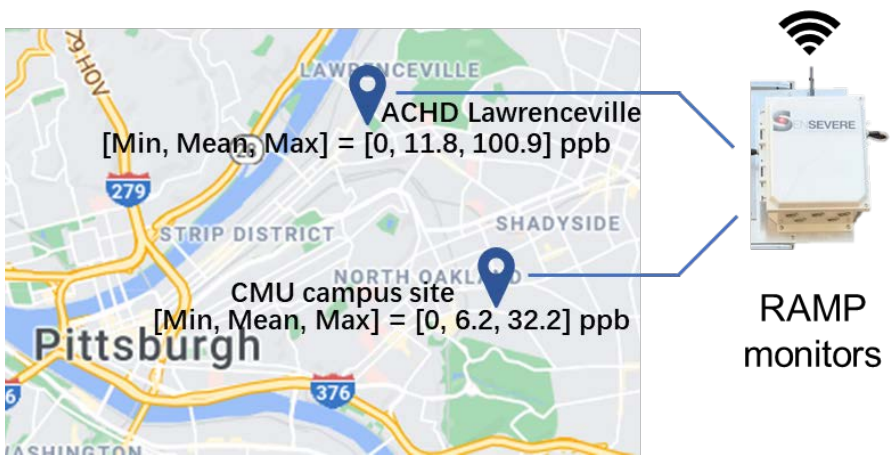

Figure S1. Locations and annual NO_2 concentrations of two reference monitoring sites – ACHD Lawrenceville and CMU campus site.

2. Limit of blank as a function of sensor age

The limit of blank (LOB) of the Alphasense NO_2 sensors was calculated to evaluate sensor applicability for atmospheric sampling. LOBs were calculated based on Eq. (S1).[1] LOB represents the sensor response to near-zero concentration samples and can be further used to calculate the limit of detection (LOD) and limit of quantification (LOQ).[1-2]

$$LOB_{i,t} = mean_{blank,i,t} + 1.645(SD_{blank,i,t}) \tag{S1}$$

Since ambient NO_2 rarely reaches 0 ppb, we revised the definition of "blank samples" as reference NO_2 concentrations between 0-2 ppb. Such an expanded range increased data available for LOB calculations. LOBs were calculated for each individual sensor *i*, at collocation period *t*, based on blank samples with a 15-minute sampling interval. The concentration average of blank samples ($mean_{blank,i,t}$) and the standard deviation of blank samples ($SD_{blank,i,t}$) were calculated based on NO_2 concentrations (ppb) derived from sensor raw signals (mV).

Two methods were used to convert sensor raw signals to NO_2 concentrations, the linear regression model and the baseline random forest (RF) model. For the linear regression model, only the original calibration model (based on the first collocation if it happened within 200 days of unpacking, with $R^2 > 0.8$) was used to calculate NO_2 concentrations from the rest of the collocation data. We also want to show the improvement in sensor performance if we regularly collocate sensors and calibrate them with advanced algorithms. Therefore, for the RF model, an individual calibration model was trained for each collocation dataset to calculate NO_2 concentrations from sensor raw signals, similar to individual calibration models reported in Malings et al. 2019.[3] LOBs calculated from RF models represent sensors that were regularly collocated over their deployment lifetime and calibrated with advanced algorithms. If a sensor does not have the qualified original calibration model, original calibration models of sensors from the same batch are averaged and applied to the collocation data, which is similar to the generalized calibration models reported in Malings et al. 2019. LOBs calculated from linear regressions represent that sensors were only collocated once or not collocated, and their results were calibrated with a simple algorithm.

Fig. S2 shows the LOB of each collocation dataset inverted from both the linear regression and the baseline RF model, shown as solid dots and hollow dots, respectively. Dots are colored based on batch numbers. The two dotted lines are the 1st and 3rd quartile of hourly NO_2 concentrations at ACHD Lawrenceville. The dashed line is the annual average NO_2 concentration at ACHD Lawrenceville.

As expected, LOBs inverted from the linear regression model increase over deployment time. This is indicative of the worsening data quality due to sensor aging described above. After approximately 200 to 400 days, the LOBs from the linear regression exceed the 3rd quartile of NO_2 concentrations at ACHD Lawrenceville. High LOBs show that these sensors cannot guarantee reliable data quality in the atmospheric sampling after long-term field deployment if they are not frequently collocated and calibrated. Thus, frequent collocation and calibration are essential to ensure reliable data quality in long-term deployment. Future research should investigate strategies to calibrate sensors with regional air quality data or satellite data instead of labor-intensive physical collocation.[4]

LOBs inverted from baseline RF models are stable around the 1st quartile of hourly NO_2 concentrations at ACHD Lawrenceville. These LOBs are much lower than those inverted from linear regressions and remain low even after very long deployments (>400 days). As previously shown by Zimmerman et al. (2018), the random forest model for NO_2 can be influenced by NO_2, CO, T, and RH, (these results were for relatively newer sensors);[5] in a city, the major NO_2 source (vehicular traffic) also co-emits CO. Thus, even though the sensors nominally perform well, the output of the RF model is not indicative of the actual sensor performance. The RF model can provide reasonable results even if the raw signals from these sensors have almost no correlation with ambient NO_2 concentrations.

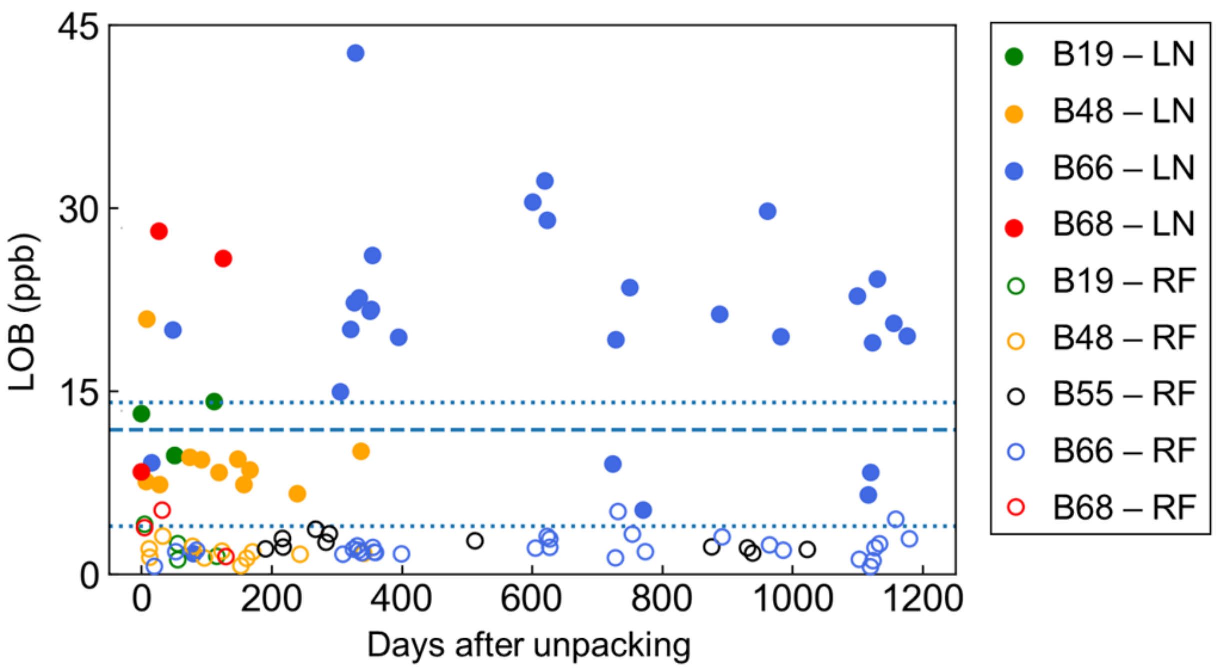

Figure S2. Solid dots and hollow dots are the limit of blanks (LOBs) calculated from linear regressions and baseline RF models. The dotted lines are the 1st and 3rd quartile of ACHD NO_2 concentrations, and the dashed line is the mean of their annual average. Sensor aging gradually increases the detection threshold, and regular collocation and advanced algorithms can ease the aging issue.

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