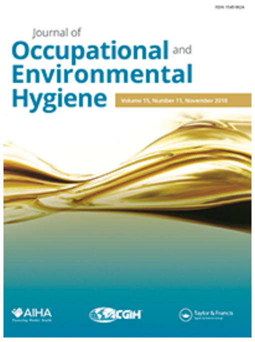

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Assessing the accuracy of commercially available gas sensors for the measurement of ambient ozone and nitrogen dioxide

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ABSTRACT
The objective of the National Institute for Occupational Safety and Health (NIOSH) accuracy criterion is to ensure that measurements from monitoring devices are within ±25% of the true concentration of the analyte with 95% certainty. To determine whether NO_2 and O_3 sensors meet this criterion, three commercially available units (Cairclip O_3/NO_2, Aeroqual NO_2, and Aeroqual O_3 sensors) were co-located three times with validated instruments (NO_x chemiluminescence [NO_{2mon}] and photometric O_3 analyzers [O_{3mon}]) at an outdoor monitoring station. As cofactors of sensor performance such as temperature (T) and relative humidity (RH) potentially influence the response of NO_2 and O_3 sensors, corrections for cofactors were made by using T, RH, and the sensor measurements to predict measurements made by NO_{2mon} and O_{3mon} during the first co-location period (training dataset). The developed models were tested in the merged data obtained from the second and third co-location periods (testing dataset). In the training and testing datasets, the mean NO_2 as measured by NO_{2mon} was 4.6 ppb (range = 0.4–35 ppb) and 9.4 ppb (range = 1–37 ppb), respectively. The mean O_3 in the training and testing datasets as measured by O_{3mon} was 38.8 ppb (range = 1–65 ppb) and 35.7 ppb (range = 1–61 ppb), respectively. None of the sensor measurements in the training dataset were within the NIOSH accuracy criterion (mean error ≥25%). After correcting for cofactors of sensor performance, the accuracy of the Cairclip O_3/NO_2 and the Aeroqual O_3 sensors considerably improved when tested with the testing dataset (mean error = -1% and 14%, respectively). However, the Aeroqual NO_2 sensor had an error that was not within ±25%. Raw measurements from the tested sensors may be unsuitable for assessing workers' exposure to NO_2 and O_3. Corrections for cofactors of Cairclip O_3/NO_2 and Aeroqual O_3 sensor performance are required for more accurate occupational exposure assessment.

KEYWORDS
Aeroqual; Cairclip; direct-reading instruments; low-cost sensors

Introduction

Nitrogen dioxide (NO_2) and ground-level ozone (O_3) are common air pollutants associated with adverse respiratory health effects.[1–8] Due to the emission of NO_2 from vehicular exhausts,[9] NO_2 is regarded as a traffic-related air pollutant, whereas O_3 is formed through photochemical reactions involving NO_x (nitrogen oxides) and volatile organic compounds,[10,11] which are emitted from vehicular exhausts. Consequently, traffic control workers may have elevated levels of exposure to NO_2 and O_3, which may be associated with lower lung function and increased respiratory symptoms.[12–14] As a result of emissions from the exhausts of internal combustion engines, other outdoor workers such as toll booth workers,[15] commercial drivers,[13,16] petrol-pump workers,[17] air cargo handlers,[18] tunnel construction workers,[19] and street cleaners[20,21] may also be exposed to higher levels of NO_2 and O_3 than the general population. The lowest occupational exposure limit (OEL) for NO_2 and O_3 are the threshold limit values (TLVs): 200 ppb for NO_2,[22] and 50–200 ppb for O_3 (depending on working conditions).[23] In most typical outdoor scenarios, outdoor workers in countries that have enforceable regulatory ambient air quality standards are likely to have occupational exposure to outdoor NO_2 and O_3 below OEL. However, some indoor workers in developed countries and indoor/outdoor workers in developing countries can have NO_2 and O_3 exposures that exceed OELs. Examples are indoor ice skating workers in rinks that use petroleum-based fuels in the resurfacers to maintain ice[24,25] and accidental release of O_3 in pulp mills.[26] Thus, reliable NO_2 and O_3 monitoring devices are needed for occupational exposure assessment.

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In contrast to traditional passive samplers for NO_2 and O_3,[27,28] electronic gas sensors are relatively new direct reading instruments that are used for assessing exposure to NO_2 and O_3. They are sometimes referred to as "low-cost sensors" because of their relatively affordable price (<$1,500). Researchers have questioned the accuracy of NO_2 and O_3 sensors, mainly because cofactors such as reactive pollutants, temperature, and relative humidity can influence the response of the sensors to NO_2 and O_3 concentrations.[29,30] Due to the concern about the quality of measurements from NO_2 and O_3 sensors, scientists have investigated their accuracy by co-locating them with validated instruments and utilizing Pearson correlation coefficients (r) and coefficients of determination (R^2) to assess the quality of the data.[31–33] To improve the correlation, the impact of T, RH, and reactive pollutants on sensor performance have been modeled. Applying these models, Cross et al.[32] and Zimmerman et al.[34] reported an increase in the correlation between corrected sensor measurements and measurements from validated instruments. Nevertheless, computed r and R^2 based on normality assumption may be inappropriate when the distribution of the analyte is not normally distributed.[35] According to scientists at the National Institute for Occupational Safety and Health (NIOSH), direct reading instruments for gaseous exposure assessment should measure within ±25% of the true concentration of the target analyte with 95% certainty.[36] This assessment corresponds to the 95% confidence interval (95% CI) accuracy level. To the best of our knowledge, researchers have not demonstrated that NO_2 and O_3 gas sensors meet this accuracy criterion in the field.

The United States Environmental Protection Agency (EPA) performs regulatory actions for ambient NO_2 and O_3 concentrations through Ambient Air Quality Standards.[37,38] EPA judges the accuracy of NO_2 and O_3 measuring devices by their performance in detecting NO_2 and O_3 after known concentrations are released onto the measuring devices. The EPA acceptable measurement of ambient NO_2 has a threshold of 15% coefficient of variation and bias, while that of O_3 has a threshold of 7% coefficient of variation and bias.[39] The EPA has a list of designated reference and equivalent instruments that can be used to achieve EPA acceptable measurements of ambient NO_2 and O_3.[40] This list includes NO_x chemiluminescence analyzers as a method for measuring ambient NO_2[40] and photometric O_3 analyzers as a method for measuring ambient O_3.[40,41] However, NO_2 and O_3 sensors are not included in the list as reference/equivalent instruments. A non-exhaustive list of commercially available NO_2 and O_3 sensors includes: Cairclip O_3/NO_2 sensor,[42] Aeroqual GSE NO_2 sensor,[43] Aeroqual GSS O_3 sensor,[44] MSA NO_2 detector,[45] Drager NO_2 sensor,[46] and Drager O_3 sensor.[46] The Aeroqual O_3 sensor is a metal-oxide-semiconductor ozone sensor,[44] whereas the other sensors are electrochemical sensors. Documentation from the sensor indicates that the Cairclip O_3/NO_2 sensor is capable of measuring the sum of NO_2 and O_3,[42] whereas the other sensors named are capable of measuring only their target analyte.[43–46] Based on the theory of operation presented in the scientific literature, electrochemical sensors contain electrodes which detect the current produced from a target gas undergoing a reaction in the sensor.[47,48] Metal-oxide-semiconductor gas sensors have semiconductors that detect a change in electrical resistance caused by the reaction of a sampled target gas with reducing or oxidizing gases present on the surface of the semiconductor.[49,50] There is an inherent lack of sensitivity of target gases in metal-oxide semiconductor sensors.[51]

As gas sensors are used for the same purpose as reference/equivalent instruments (i.e., to measure air pollutants relevant to health), this study examined the accuracy of three commercial NO_2 and O_3 gas sensors in the field to validate their use for occupational exposure assessment using the NIOSH accuracy criterion. Additionally, the study examined the correlation of measurements made with the gas sensors and reference/equivalent instruments.

Methods

Investigating the accuracy of NO_2 and O_3 sensors

One of each sensor [the NO_2 sensor (GSE, s500, 0-1 ppm, Aeroqual), O_3 sensor (GSS, s500, 0–0.15 ppm, Aeroqual) and the O_3+NO_2 sensor (O_3/NO_2, Cairclip, Cairpol)] was co-located outdoors three times side-by-side with the Southwest Ohio Air Quality Agency monitoring station (250 William Howard Taft Rd., Cincinnati, OH). All the sensors were factory calibrated by the manufacturers, and zero calibration was performed on the Aeroqual sensors by the study team. The factory calibration of the Cairclip O_3/NO_2 sensor is sufficient for 1 year provided that its operational conditions are adhered to.[42] Prior to the commencement of the current study, the sensors had been used for approximately 5 months since the receipt from the manufacturers. They were within the recommended 1-year factory calibration cycle given by the manufacturers. The first co-locating period was between 3 pm on 07/19/2017 to 2 pm on 07/24/2017, and the second and third co-locating periods were between 3 pm on 08/30/2017 to 2 pm on 09/01/2017 and 3 pm on 10/17/2017 to 2 pm on 10/19/2017, respectively. The sensors were deployed to compare the readings obtained from them to those of the EPA reference/equivalent instruments at the monitoring station (Figure S1). The monitoring station uses a NO_x chemiluminescence analyzer (Model T200, Teledyne) [NO_{2mon}] and a photometric O_3 analyzer (Model 400E, Teledyne) [O_{3mon}]. The recommended operating conditions of the measuring devices are −20–40°C and 10–90% RH for the Cairclip O_3/NO_2 sensor, 0–40°C and 15–90% RH for the Aeroqual NO_2 sensor, and 0–40°C and 10–90% RH for the Aeroqual O_3 sensor, 5–40°C and 0–95% RH for the NO_x chemiluminescence analyzer, 5–40°C and 0–90% RH for the photometric O_3 analyzer.[43,44,52–54] Data from the NO_x chemiluminescence analyzer and photometric O_3 analyzer were added together to obtain "reference O_3+NO_2." The limits of detection (LOD) of the measuring devices were obtained from their manuals (20 ppb for the Cairclip O_3/NO_2 sensor, 5 ppb for the Aeroqual NO_2 sensor, 1 ppb for the O_3 sensor, 0.4 ppb for the NO_x chemiluminescence analyzer and 0.6 ppb for the photometric O_3 analyzer).[43,44,52–54]

Temperature (T) and relative humidity (RH) were simultaneously measured with a temperature/relative humidity monitor (O83E, Met One Instruments, Inc.). The time and date on all devices were synchronized and were set to record measurements every minute. For quality assurance, data from the reference/equivalent instruments were reviewed by the operators of the monitoring station (Southwest Ohio Air Quality Agency). At the end of the sampling period, hourly averages of NO_2, O_3, T, and RH were provided by the operators of the monitoring station.

All the data logged per minute by the sensors (including data < LOD) were downloaded to a computer using the manufacturers' proprietary software, and hourly averages of NO_2 and O_3 levels measured by the sensors were calculated. Data obtained from the reference/equivalent instruments at the monitoring station were regarded as the "gold standards" providing the true concentration of ambient NO_2 and O_3. Data from all measurements were imported into R Studio[55] for data analysis. Only hourly averaged measurements ≥ the LOD of the sensors and reference instruments were used in this study. First, accuracy was determined by estimating the error associated with measurements of the NO_2 and O_3 sensors. This was achieved by creating variables that contained the percentage difference between the measurements made by the sensors and measurements from the reference instruments (Equation (1)):

$$Error = \left(\frac{Sensor\ measurements_i - Reference\ instrument\ measurements_i}{Reference\ instrument\ measurements_i}\right) \times 100, \tag{1}$$

where i = individual observation in the dataset.

Second, the mean error was calculated and a bias-corrected and accelerated (BCa) bootstrap method was used to calculate 95% CI for the mean error.[56–59] Bootstrap was employed for the calculation of 95% CI because the created error variables were non-normal. Accuracy was defined as having a 95% CI of mean error (lower 95% CI of mean error < true mean error < upper 95% CI of mean error) within -25 to +25%.

The correlation of measurements from the sensors and reference instruments were also calculated in order to make results from the current study comparable to results of existing studies. The following tests for accuracy and correlation of the sensor measurements compared to the O_3 reference-equivalent instrument (O_{3mon}), NO_2 reference instrument (NO_{2mon}) and $(O_3+NO_2)_{mon}$ were carried out:

- Aeroqual O_3 sensor and O_{3mon};
- Aeroqual NO_2 sensor and NO_{2mon}; and
- Cairclip O_3/NO_2 sensor and $(O_3+NO_2)_{mon}$.

Developing corrective models

Data from the first co-locating period were utilized to develop regression models to correct for measured cofactors of sensor performance that potentially interfere with the accuracy of the sensors. The data collected during this period is described as the "Training Dataset." To develop a model to correct for measured cofactors of the Aeroqual O_3 sensor performance, and to correct for the inherent error in the Aeroqual O_3 sensor, measurements of T, RH, NO_{2mon}, and the Aeroqual O_3 sensor were used to predict O_{3mon} (Equation (S1) is available in online supplemental materials). Due to the nonlinear

Table 1. Summary of measurements in the training dataset.

	T (°C)	RH (%)	O_{3mon} (ppb)	Aeroqual O_3 (ppb)	NO_{2mon} (ppb)	Aeroqual NO_2 (ppb)	$(O_3+NO_2)_{mon}$ (ppb)	Cairclip O_3/NO_2 (ppb)
Minimum	21.9	39.0	1.0	1.7	0.4	7.6	21.0	31.6
Maximum	34.5	90.0	65.0	69.7	35.0	92.9	69.0	187.6
Mean	27.4	69.8	38.8	43.1	4.6	30.5	43.4	70.0
SD	4.0	13.5	14.5	14.9	6.0	11.3	11.4	24.5
n	120	120	120	107	120	120	120	120

Measurements are based on hourly averages, training dataset = data used to develop the regression models. O_{3mon} = O_3 measured by the EPA reference-equivalent instrument with a photometric O_3 analyzer, Aeroqual O_3 = O_3 measured by the Aeroqual GSS O_3 sensor, NO_{2mon} = NO_2 measured by the EPA reference instrument with a NO_x chemiluminescence analyzer, Aeroqual NO_2 = NO_2 measured by the Aeroqual GSE NO_2 sensor, $(O_3+NO_2)_{mon}$ = the sum of NO_2 and O_3 measured by the EPA reference instruments, Cairclip O_3/NO_2 = O_3+NO_2 measured by the Cairclip O_3/NO_2 sensor, n = number of observations.

response of metal-oxide semiconductor sensors to the target gas and cofactors of sensor response,[51] quadratic terms were added to the independent variables. Variable selection was performed with a stepwise regression model using the minimum Akaike Information Criterion (AIC) for model selection. To develop a model to correct the effect of measured cofactors of the Aeroqual NO_2 sensor performance, and to correct for the inherent error in the Aeroqual NO_2 sensor, measurements of T, RH, O_{3mon}, and the Aeroqual NO_2 sensor were used to predict NO_{2mon} (Equation (S2)). Last, to develop a model to correct the effect of measured cofactors of the Cairclip O_3/NO_2 sensor performance, and to correct for the inherent error in the Cairclip O_3/NO_2 sensor, measurements of T, RH, and the Cairclip O_3/NO_2 sensor were used to predict $(O_3 + NO_2)_{mon}$ (Equation (S3)). After developing the regression models as described, the independent variables that were not significant ($P > 0.05$) were removed from the models, and the final models were used to correct the raw sensor data in the subsequent field trial.

Testing the models developed

The sensors were co-located at the monitoring station twice to test whether the accuracy of the sensor measurements could be improved by utilizing the regression coefficients obtained from the final models. The data obtained to test the models (testing dataset) were collected from the second and third co-locating periods. These data were merged together to form one testing dataset. Measurements from the testing dataset were multiplied by the corresponding coefficients obtained from the final models.

Errors of the corrected sensor measurements were calculated as described in Equation (1), and mean errors and 95% CI were calculated. In addition, the R^2 of the measurements from the reference instruments and the corrected sensor measurements were calculated.

Results

Summary of measurements

In the training dataset, 10.8% of hourly averaged measurements made by the Aeroqual O_3 sensor were < its LOD of 1 ppb. In the testing dataset, 42.9% of hourly averaged measurements made by the Aeroqual NO_2 sensor were < its LOD of 5 ppb, and 34.1% of hourly averaged measurements from the Aeroqual O_3 sensor were < its LOD of 1 ppb. Other sensor measurements were within their LOD. Hourly averaged data < LOD were removed.

Tables 1 and 2 present the summary statistics of hourly averaged NO_2, O_3, O_3+NO_2, T, and RH from the reference instruments and sensors in the training and testing datasets. In the training dataset (i.e., the dataset used to develop the regression models), ambient T ranged from 21.9–34.5°C, and ambient RH ranged from 39–90%. In the testing dataset (i.e., the dataset used to test the developed regression models), ambient T ranged from 7.4–28.4°C, and ambient RH ranged from 35–87%. The T and RH values were within the operating conditions specified by the manufacturers. The mean NO_2 as measured by NO_{2mon} was 4.6 ppb (range = 0.4–35 ppb) in the training dataset and 9.4 ppb (range = 1–37 ppb) in the testing dataset. Furthermore, the mean O_3 concentration as measured by O_{3mon} was 38.8 ppb (range = 1–65 ppb) in the training dataset and 35.7 ppb (range = 1–61 ppb) in the testing dataset.

Accuracy and correlation during the first co-location period

Table 3 and Figure S2 present the results obtained from the first co-location of the sensors with reference instruments at the monitoring station. During the first co-locating period, when the sensors were deployed to obtain data for the corrective models, there was a consistent positive bias in sensor measurements. Results of raw measurements from the Aeroqual O_3 sensor when compared to O_{3mon} had a mean error of 30%

Table 2. Summary of measurements in the testing dataset.

	T (°C)	RH (%)	O_{3mon} (ppb)	Aeroqual O_3 (ppb)	NO_{2mon} (ppb)	Aeroqual NO_2 (ppb)	$(O_3+NO_2)_{mon}$ (ppb)	Cairclip O_3/NO_2 (ppb)
Minimum	7.4	35.0	1.0	1.4	1.0	5.2	21.0	21.9
Maximum	28.4	87.0	61.0	63.1	37.0	31.2	68.0	86.1
Mean	17.5	64.5	35.7	33.1	9.4	15.0	45.1	47.3
SD	5.8	15.2	14.9	17.6	7.7	7.6	12.0	12.8
n	91	91	91	60	91	52	91	91

Measurements are based on hourly averages, testing dataset = data used to test the developed regression models. See footnotes of Table 1.

Table 3. Accuracy and correlation of raw data from the NO_2 and O_3 sensors obtained from the training dataset (data used to develop the regression models).

s/n	Comparison	n	R^2	Mean error	95% CI of mean error	Within NIOSH accuracy criterion
A	Aeroqual O_3 vs. O_{3mon}	107	0.71	30%	13–78%	No
B	Aeroqual NO_2 vs. NO_{2mon}	120	0.03	4264%	3160–5662%	No
C	Cairclip O_3/NO_2 vs. $(O_3+NO_2)_{mon}$	120	0.32	65%	58–76%	No

n = number of observations, R^2 = coefficient of determination based on linear regression, mean error = percent difference between the measurements made by the sensors and measurements from the reference instruments (equation 1), 95% CI of mean error was obtained from BCa bootstrap confidence intervals, NIOSH accuracy criterion refers to 95% CI estimated mean error of ±25%, Aeroqual O_3 = O_3 measured by the Aeroqual GSS O_3 sensor, O_{3mon} = O_3 measured by the EPA reference-equivalent instrument with a photometric O_3 analyzer, Aeroqual NO_2 = NO_2 measured by the Aeroqual GSE NO_2 sensor, NO_{2mon} = NO_2 measured by the EPA reference instrument with a NO_x chemiluminescence analyzer, Cairclip O_3/NO_2 = O_3+NO_2 measured by the Cairclip O_3/NO_2 Sensor, $(O_3+NO_2)_{mon}$ = the sum of NO_2 and O_3 measured by the EPA reference instruments.

(95% CI = 13, 78) (Table 3, Row A, and Figure S2 A and B). The variation in raw measurements of the Aeroqual O_3 sensor explained 71% of the variation in O_{3mon}.

Raw measurements from the Aeroqual NO_2 sensor when compared to NO_{2mon} had a mean error of 4264% (95% CI = 3160, 5662) (Table 3, Row B, and Figure S2 C and D). The variation in raw measurements of the Aeroqual NO_2 sensor explained only 3% of the variation in NO_{2mon}. Raw measurements from the Cairclip O_3/NO_2 sensor when compared to $(O_3+NO_2)_{mon}$ had a mean error of 65% (95% CI = 58, 76) (Table 3, Row C, and Figure S2 E and F). Furthermore, the variation of raw measurements of the Cairclip O_3/NO_2 sensor explained 32% of the variation in $(O_3+NO_2)_{mon}$.

It appeared that higher RH and lower T were associated with lower measurements of O_3 and NO_2 (Figure S2). However, results of the variable selection for the final model showed that the effect of T on NO_{2mon} or O_{3mon} was not significant (results not shown). Consequently, T was not included in the final models (Table 4).

The final model for correcting the measured cofactors of the Aeroqual O_3 sensor performance included the following independent variables: The Aeroqual O_3 sensor squared, NO_{2mon} and RH^2 (relative $humidity^2$) (Table 4A). In the model developed, measurements of Aeroqual O_3 sensor and RH had a nonlinear relationship with O_{3mon} (Table 4A).

The final model for correcting the measured cofactors of the Aeroqual NO_2 sensor performance included the measurements of the Aeroqual NO_2 sensor, O_{3mon}, and RH as independent variables (Table 4B). One ppb increase in NO_2 measured by the Aeroqual NO_2 sensor was associated with 0.1 ppb increase in NO_{2mon} (Table 4B).

Last, the final model for correcting the measured cofactors of the Cairclip O_3/NO_2 sensor performance included the measurements of the Cairclip O_3/NO_2 sensor and RH as independent variables (Table 4C). One ppb increase in O_3+NO_2 measured by the Cairclip O_3/NO_2 sensor was associated with 0.1 ppb increase in $(O_3+NO_2)_{mon}$ (Table 4C).

Accuracy and correlation in the testing dataset and obtaining corrected readings from the sensors

Table 5 and Figures S3–S5 presents the results obtained from co-locating the sensors with reference instruments at the monitoring station in the testing dataset. Prior to the correction of the Aeroqual O_3 sensor, raw measurements of the Aeroqual O_3 sensor when assessed for accuracy against O_{3mon}, had a mean error of -9% (95% CI = -18, 3) in the testing dataset (Table 5, Row A, and Figure S3 A and B). After testing the corrective model that controlled for measured cofactors of the Aeroqual O_3 sensor performance (NO_2 and RH) and the inherent error in the measurements, the corrected measurements of the Aeroqual O_3 sensor when assessed for accuracy against O_{3mon}, had a mean error of -1% (95% CI = -14, 9) (Table 5, Row A, and Figure S3 C and D). Prior to the correction, the variation of raw measurements from the

Table 4. Results of the models for correcting the effect of measured cofactors of sensor performance.

A. Aeroqual O_3 Sensor[A]			B. Aeroqual NO_2 Sensor[B]			C. Cairclip O_3/NO_2 Sensor[C]		
Parameters	Regression estimate	P-value	Parameters	Regression estimate	P-value	Parameters	Regression estimate	P-value
Intercept	46.974	< 0.001	Intercept	37.149	< 0.001	Intercept	70.474	< 0.001
$(\text{Aeroqual } O_3)^2$	0.005	< 0.001	Aeroqual NO_2	0.147	< 0.001	Cairclip O_3/NO_2	0.139	< 0.001
NO_{2mon}	−0.936	< 0.001	O_{3mon}	−0.518	< 0.001	–		
$(RH)^2$	−0.003	< 0.001	RH	−0.245	< 0.001	RH	−0.534	< 0.001

[A] response variable = O_{3mon}, $R^2 = 0.87$ [B] response variable = NO_{2mon}, $R^2 = 0.66$ [C] response variable = $(O_3+NO_2)_{mon}$, $R^2 = 0.69$
[A] result of equation S1 (n = 107) [B] result of equation S2 (n = 120) [C] result of equation S3 (n = 120)
See Table 3 for other footnotes.

Table 5. Accuracy and correlation of corrected NO_2 and O_3 sensor readings obtained from the testing data set (data used to test the regression models).

s/n	Comparison	n	Action	R^2	Mean error	95% CI of mean error	Within NIOSH accuracy criterion
A.	Aeroqual O_3 vs. O_{3mon}	60	Raw	0.74	−9%	−18–3%	Yes
			Testing model in Table 4A	0.80	−1%	−14–9%	Yes
B.	Aeroqual NO_2 vs. NO_{2mon}	52	Raw	0.08	150%	98–212%	No
			Testing model in Table 4B	0.24	−30%	−48 – -10%	No
C.	Cairclip O_3/NO_2 vs. $(O_3+NO_2)_{mon}$	91	Raw	0.63	24%	20–29%	No
			Testing model in Table 4C	0.65	14%	9–18%	Yes

See Table 3 for footnotes.

Aeroqual O_3 sensor explained 74% of the variation of O_{3mon} in the testing dataset. After correction, the variation of the corrected Aeroqual O_3 sensor measurements explained 80% of the variation of O_{3mon}.

The raw measurements of the Aeroqual NO_2 sensor when assessed for accuracy against NO_{2mon}, had a mean error of 150% (95% CI = 98, 212) in the testing dataset (Table 5, Row B, and Figure S4 A and B). After controlling for measured cofactors (O_3 and RH) and the inherent error in the measurements, the corrected measurements of the Aeroqual NO_2 sensor when assessed for accuracy against NO_{2mon}, had a mean error of -30% (95% CI = −48, −10) (Table 5, Row B, and Figure S4 C and D). The variation of raw measurements from the Aeroqual NO_2 sensor explained only 8% of the variation of NO_{2mon}. After correction, the variation of the corrected Aeroqual NO_2 sensor measurements explained 24% of the variation of NO_{2mon}.

The raw measurements of the Cairclip O_3/NO_2 sensor when assessed for accuracy against $(O_3+NO_2)_{mon}$, had a mean error of 24% (95% CI = 20, 29) in the testing dataset (Table 5, Row C, and Figure S5 A and B). After controlling for RH and the inherent error in the sensor measurements, the corrected measurements of the Cairclip O_3/NO_2 sensor when assessed for accuracy against $(O_3+NO_2)_{mon}$, had a mean error of 14% (95% CI = 9, 18) (Table 5, Row D, and Figure S5 C and D). The variation of raw measurements from the Cairclip O_3/NO_2 sensor explained 63% of the variation of $(O_3+NO_2)_{mon}$. After correction, the variation of the corrected Cairclip O_3/NO_2 sensor measurements explained 65% of the variation of $(O_3+NO_2)_{mon}$.

Discussion

Results from this study show that none of the measurements of the three tested sensors, except for the Aeroqual O_3 sensor in the testing dataset, had a 95% CI of mean error within ±25%. Thus, for the raw sensor measurements, only the Aeroqual O_3 sensor measurements in the testing dataset were within the NIOSH accuracy criterion (95% CI of the mean error = −18–3%). However, in the training dataset, the Aeroqual O_3 sensor had a 95% CI of the mean error ranging from 13–78% (outside ±25%). Because 25% is included in the observed 13–78% range, the data show that the accuracy of the Aeroqual O_3 sensor is varied, and may be accurate only under specific conditions. After controlling for NO_2, RH, and the inherent error in the Aeroqual O_3 sensor measurements, corrected measurements of the Aeroqual O_3 sensor improved in accuracy (mean error = -1%). This finding suggests that utilizing a calibration model that controls the effect of RH and NO_2 on the performance of the Aeroqual O_3 sensor may be required prior its use for occupational exposure assessment. The inaccurate results of the raw sensor measurements may not be due to sensor drift, as the sensors were within the recommended annual factory calibration cycle given by the manufacturers.

Comparison of measurements of the Cairclip O_3/NO_2 sensor with ambient O_3+NO_2 concentrations after controlling for RH and the inherent error in the sensor measurements showed accurate results (mean error = 14% [95% CI = 9–18%]). Conversely, measurements of the Aeroqual NO_2 sensor were not accurate, even after controlling for cofactors of the Aeroqual NO_2 sensor performance and the inherent error in measurements. The data suggest that Aeroqual NO_2 sensor may not be an accurate instrument for monitoring outdoor NO_2 exposures.

Because RH was a significant cofactor of the sensors performance and T was as not, the impact of varying levels of RH on the sensors performance is more important than fluctuating T. This indicates that RH needs to be measured in parallel with the Aeroqual O_3 and Cairclip O_3/NO_2 sensors when they are used for exposure assessment. In addition, simultaneous measurements of NO_2 may be needed when the Aeroqual O_3 sensor is deployed for measurements. As controlling for the effect of varying levels of RH was sufficient enough to make the Cairclip O_3/NO_2 sensor measurements within ±25% of O_3+NO_2, it is possible that the Cairclip O_3/NO_2 sensor measures accurately in environments that have low RH variation.

Our results show unequal variance of the tested sensors when compared to the corresponding reference instruments. In the training dataset, O_{3mon} and the Aeroqual O_3 sensor had similar standard deviations [SD] (~15 ppb). However, this was not the case in the testing dataset (O_{3mon} SD ~15 ppb and Aeroqual O_3 SD ~18 ppb). Furthermore, the SD of NO_{2mon} and the Aeroqual NO_2 sensor were markedly different in the training dataset, but approximately equal (8 ppb) in the testing dataset. Similarly, the Cairclip O_3/NO_2 sensor and the reference $(O_3+NO_2)_{mon}$ instruments had markedly different SD in the training dataset, but similar SD in the testing dataset. The data clearly show that the performance of the sensors is influenced by environmental conditions such as RH, which was controlled in the corrective models. However, it must be noted that other unmeasured cofactors of the sensors performance may exist.

Zimmerman et al. discovered that the response of one electrochemical NO_2 sensor (Alphasense ID: NO_2-B43F) was influenced by T, RH, CO, CO_2, SO_2, and O_3.[34] In that same study, RH had the greatest impact on the response of the NO_2 sensor in comparison to T, CO, CO_2, SO_2, and O_3.[34] In the current study, the linear regression model developed for the Aeroqual NO_2 sensor showed that the effect of O_3 on the performance of the Aeroqual NO_2 sensor was the greatest (i.e., greater magnitude of regression coefficient for O_3 in comparison to RH). This difference between the current study and that of Zimmerman et al.[34] could be due to the use of different NO_2 sensors (i.e., Alphasense ID: NO_2-B43F versus the Aeroqual NO_2 sensor) that have different levels of sensitivity to cofactors (RH and O_3, for example). RH values in the study by Zimmerman et al. was not reported, however, O_3 concentration was approximately 0–42 ppb,[34] and 1–65 ppb in the current study.

Other researchers have also reported the effects of cofactors of electrochemical sensor performance in the field.[32,33] Although controlling the influence of cofactors of sensor performance has been shown to improve the correlation of the corrected sensor measurements to reference/equivalent instruments, previous studies did not include comparison to the NIOSH ±25% accuracy criterion.[32–34] Therefore, it is unclear whether the tested sensors in the quoted studies[32–34] are suitable for the use of occupational exposure assessment. Furthermore, the practical benefit of the sensors for exposure assessment may not be economical, given that measurements from other monitoring devices such as reference instruments are required to obtain accurate measurements using corrective models. To obtain accurate measurements from so-called low-cost sensors, modifications in hardware and operating technique may be required.

Limitations

We used relatively short co-locating periods for the instruments. Nevertheless, hourly fluctuations of T and RH during the three co-locating periods were representative of different weather conditions (for the seasons that we measured). As a result, we were able to assess the accuracy of the sensors in the field during different representative outdoor conditions. Restricting our analysis to measurements ≥ LOD of the tested sensors can potentially cause a selection bias where data analyzed are not representative of environmental conditions associated with very low (i.e., < LOD) sensor measurements. However, this method was employed in the current study in order to attain an unequivocal assessment of the performance of the tested sensors in the field. The operators of the monitoring station were only able to provide hourly averages of NO_2 and O_3, and for this reason the removal of measurements < LOD were made after calculating hourly averages. The removal of raw measurements (i.e., data logged per minute) < LOD is a more conservative approach to ensure the validity of data. Finally, the only potentially interfering cofactors that we measured were RH and T; there may be additional contributions from other atmospheric pollutants.

Conclusions

Raw measurements from the Aeroqual O_3 and NO_2 and Cairclip O_3/NO_2 sensors may be unsuitable for exposure assessment of outdoor workers such as traffic controllers, toll booth workers, and commercial drivers. Utilizing models to correct for cofactors of sensor performance are required to ensure accurate occupational exposure assessment. The practical benefit of these so-called low-cost sensors may not be economical, given that measurements from other monitoring devices such as reference/equivalent instruments are required to obtain accurate measurements from corrective models.

Recommendations

We recommend co-locating NO_2 and O_3 sensors with validated reference instruments to investigate the accuracy of sensor measurements before using them for occupational exposure assessment.

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