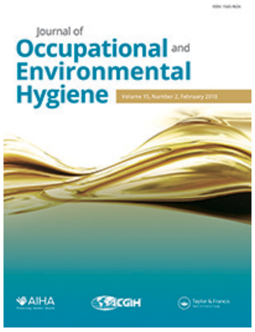

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Evaluation of low-cost electro-chemical sensors for environmental monitoring of ozone, nitrogen dioxide, and carbon monoxide

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ABSTRACT

Development of an air quality monitoring network with high spatio-temporal resolution requires installation of a large number of air pollutant monitors. However, state-of-the-art monitors are costly and may not be compatible with wireless data logging systems. In this study, low-cost electro-chemical sensors manufactured by Alphasense Ltd. for detection of CO and oxidative gases (predominantly O_3 and NO_2) were evaluated. The voltages from three oxidative gas sensors and three CO sensors were recorded every 2.5 sec when exposed to controlled gas concentrations in a 0.125-m^3 acrylic glass chamber. Electro-chemical sensors for detection of oxidative gases demonstrated sensitivity to both NO_2 and O_3 with similar voltages recorded when exposed to equivalent environmental concentrations of NO_2 or O_3 gases, when evaluated separately. There was a strong linear relationship between the recorded voltages and target concentrations of oxidative gases ($R^2 > 0.98$) over a wide range of concentrations. Although a strong linear relationship was also observed for CO concentrations below 12 ppm, a saturation effect was observed wherein the voltage only changes minimally for higher CO concentrations (12–50 ppm). The nonlinear behavior of the CO sensors implied their unsuitability for environments where high CO concentrations are expected. Using a manufacturer-supplied shroud, sensors were tested at 2 different flow rates (0.25 and 0.5 Lpm) to mimic field calibration of the sensors with zero air and a span gas concentration (2 ppm NO2 or 15 ppm CO). As with all electrochemical sensors, the tested devices were subject to drift with a bias up to 20% after 9 months of continuous operation. Alphasense CO sensors were found to be a proper choice for occupational and environmental CO monitoring with maximum concentration of 12 ppm, especially due to the field-ready calibration capability. Alphasense oxidative gas sensors are usable only if it is valuable to know the sum of the NO_2 and O_3 concentrations.

KEYWORDS
Air quality; field calibration; gas sensors; monitoring network

Introduction

The development of an effective air quality monitoring network is of great need for researchers and environmental protection authorities. Knowledge regarding the spatial variability of the air pollutants' concentrations within an air quality monitoring network has several advantages including: (1) to compare the monitored levels and standards set by the Environmental Protection Agency (USEPA) and Occupational Safety and Health Administration (OSHA); (2) to assess the risk of exposure to the monitored air pollutants; and (3) to mitigate and control emissions from known sources.[1,2] Ozone (O_3), nitrogen dioxide (NO_2), and carbon monoxide (CO) are 3 out of 6 criteria air pollutants designated by the USEPA.[3] Ambient concentrations of the criteria air pollutants should comply with the national ambient air quality standards (NAAQS) regulated by the USEPA.

Ozone is a strong oxidant with highly variable ambient concentrations that are associated with urbanization and industrialization of the environment.[4] Ground level O_3 in ambient air causes inflammation, reduced lung function, DNA damage, and increased symptoms and development of asthma.[5,6] In occupational settings, O_3 is the main air pollutant product of arc welding processes (steady-state concentration of 180 ppb during regular arc welding).[7] Ground level O_3 is associated with both acute

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and chronic health concerns. Within the first few hours after the O_3 exposure, changes in lung capacity, epithelial permeability, and reactivity to bronchoalveolar airways are anticipated.[8] Chronic health effects of the exposure to O_3 include alterations in function, deterioration, and premature aging of the lungs.[9] The regulated permissible exposure limit by OSHA (PEL, concentration to which individuals can be continuously exposed in a normal 8-hr workday) measured as a time weighed average (TWA) exposure to O_3 is 100 ppb TWA.[10] The NAAQS in 2015 restricts the acceptable concentration of outdoor O_3, averaged over 8 hr, to 70 ppb.[3]

NO_2 emissions are common from thermal processes, combustion, vehicle exhaust, and fertilizers. The diverse group of NO_2 emitters makes NO_2 a common air pollutant in most industries.[11] The acute health effects of NO_2 are diverse and include irritation of eyes, throat, and lungs. Chronic exposure to NO_2 increases prevalence of asthma and has the potential outcome of obliterative bronchiolitis.[5] The health impacts of NO_2 are intensified at higher relative humidity when NO_2 and water produce nitric acid. The 8-hr PEL for NO_2 is 5 ppm according to the OSHA regulation.[10] The NAAQS for 1-hr averaging time of NO_2 is 100 ppb.[3]

CO is an odorless, ubiquitous air pollutant that is generated from the incomplete oxidation of carbon during combustion processes. Power plants, boilers, forest fires, wood pellets storage facilities, foundries, transportation, and smoking are some of the most common sources for environmental CO emission.[12] Occupationally, exposure to CO is a major hazard to those dealing with combustion of fuel. For example, fire fighters may be exposed to CO concentrations as high as 3,000 ppm.[13] The health effects of carbon monoxide range widely from minute cardiovascular and neurobehavioral effects to unconsciousness and death depending on the concentration.[14] The PEL for exposure to CO in general industry is 50 ppm (29 CFR 1910.1000 Z-1 Table).[10] The health effects of exposures to CO concentrations less than 50 ppm are also associated with impairment of the cardiovascular system and since any increase in CO concentration decreases the availability of oxygen, it directly impacts the human brain.[9,14] The NAAQS for 8-hr averaging time of CO is 9 ppm.[3]

Traditionally, air pollutants are measured using expensive and bulky instruments at fixed locations.[15] However, the concentrations of air pollutants are highly variable over both space and time.[16] Real-time and high-resolution (few meters) detection that facilitates the mapping of criteria air pollutants are important as peak exposures can lead to bad health outcomes, particularly for sensitive groups.[17] Furthermore, in occupational facilities, understanding peak exposures may help identify control strategies to reduce exposures. A high-resolution spatio-temporal air quality monitoring network would deploy a dense network of low-cost sensors (< \$100 per sensor) operating over the area of study with a fast response time. Recent advances in wireless and smart gas detection, mostly based on electro-chemical sensing, have made these sensors attractive tools for real-time monitoring of air pollutants.[18-21] Although electro-chemical sensing is common for some gases such as CO and O_2,[22] electro-chemical detection of highly variable and reactive oxidizing gases such as O_3 and NO_2 has not been evaluated thoroughly.[23]

As a response to the demand for inexpensive but ubiquitous detection of occupationally and environmentally relevant gases, low-cost sensors compatible with wireless programmed platforms have been developed by a number of companies. For example, Alphasense Co., Essex, UK has recently patented electro-chemical oxidative gas and CO sensors (see Figure 1a), which the manufacturer claims are sensitive and reliable for industrial gas detection.

On these bases, the main goal of this study was to investigate adequacy of applying low-cost electro-chemical oxidative gas and CO sensors for deployment in an air quality monitoring network. First, the performance of the sensors in comparison to reference instruments was evaluated. Then, the response time of each sensor

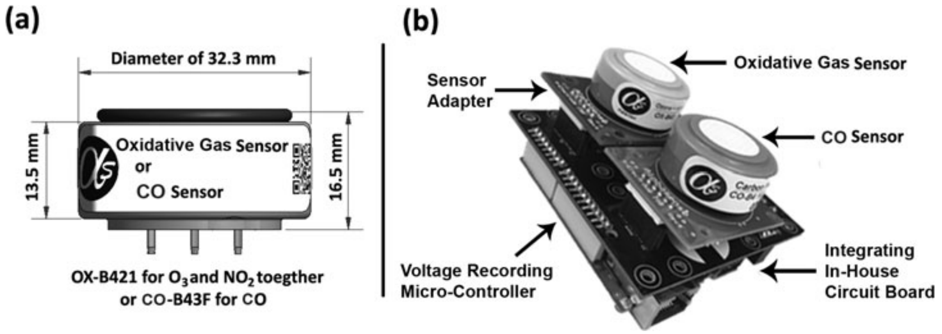

Figure 1. Low-cost electro-chemical oxidative gas and CO sensors tested in this study: (a) sizing and (b) positioning of the sensors on a custom-built circuit board.

was determined via a series of bump tests, separately for oxidative gas and CO sensors. Although electrochemical CO sensors are sensitive to hydrogenated gases (e.g., hydrogen sulfide, alcohols and hydrocarbons), an internal organic vapor filter placed at the sensor inlet reduces the interfering effects of these species. According to the manufacturer, cross sensitivity of CO sensors to potential interfering gases at different concentrations up to 5 ppm is less than 3%. In contrast, the oxidative gas sensors respond to both O_3 and NO_2. Therefore, this study also seeks to identify the response range by the oxidative gas sensors when exposed to common ranges of concentrations for each gas, separately.

Methods

Sensor node design

Each low-cost sensing unit was comprised of two sensors (one oxidative gas sensor and one CO gas sensor), two adapters (one for each sensor, made by the Alphasense Ltd.), one microcontroller for reading and storing the voltages obtained from each sensor, and a custom-built circuit to connect and integrate all constituents built in-house. The microcontroller was developed to record detected signals by the sensors as a voltage (ranging between 0 and 5 V) on a memory card every 2.5 sec. The integrated circuit board was responsible for connecting the microcontroller to the sensor adaptors and implementing the electric voltage gains. To obtain proper resolution at the concentration range of interest, the electric voltage gain, the mean ratio of the voltage signal at the output port of the circuit to that of at the input of the circuit, was 5 for the oxidative gas sensor and 1 for the CO sensor. The integrating custom-built circuit (see Figure 1b) was an Arduino Yun board (https://www.arduino.cc/en/Main/ArduinoBoardYun). Arduino is an open-source and inexpensive electronics platform with an easy programming language for fast prototyping and creation of interactive communication between the sensor and the memory card. The Yun model of Arduino board used in this study provided the advantage of direct posting the recorded voltages over an embedded webserver software. The Arduino board was powered by connection to a 5-V electric supply and had the capability for wireless connection to a computer via Wi-Fi. The integrating board included circuitry that stored and transmitted voltages detected by the sensors. The recorded voltages were stored and appended in a text file after each 2.5 sec. Then, a Visual Basic for Application (VBA) code was developed to sort and average the data over 5 min periods.

Evaluation of the oxidative gas sensors

The main purpose of evaluating the oxidative gas sensor was to correlate the recorded voltage outputs by the Alphasense oxidative gas sensors to the concentration values of either O_3 or NO_2 measured by reference monitors. The oxidative gas sensors were exposed separately to different targeted concentrations of either NO_2 or O_3 and their responsiveness to alterations in the gas concentrations was examined. All measurements were conducted inside an acrylic chamber (0.5 × 0.5 × 0.5 m), tinted to minimize interactions of O_3 with light. For statistical reliability, three units of each sensor type were tested at a time. The linearity of the response was investigated and equations describing the relationship between the sensor response voltage and concentration were developed. The choice of concentration range for each of O_3 (25–150 ppb) and NO_2 (0.2–1.5 ppm) gases was based on typical concentration of these gases in the atmosphere and in occupational environments and are all below regulated occupational exposure limits.[24]

Ozone was introduced to the chamber using a bench-top ozone generator (Model 1008-PC, Dasibi Environmental Co., Glendale, CA, USA) that irradiates ultraviolet (UV) light from a cold cathode Hg lamp on the zero air. The zero air was produced by filtering compressed house air using a combination of a HEPA filter, silica gel, purafilm, and charcoal columns. Generation of O_3 was controlled through a cycle consisting of three phases of: (1) ascending, wherein the concentration was increasing from the baseline concentration to the target concentration; (2) steady state, wherein O_3 concentration was maintained at the targeted concentration (25, 50, 75, or 100 ppb); and (3) descending, wherein the concentration was decreasing from the target concentration to the baseline concentration (Figure 3). The flow rate of the O_3 into the chamber for all experiments was adjusted to 5.5 Lpm, as suggested by the manufacturer of the O_3 generator. Before the start of each experiment, zero air was blown into the chamber at a flow rate of 10 Lpm to create the lowest possible O_3 concentration for the baseline level. The O_3 concentration was measured continuously using a bench-top O_3 analyzer (Model 1008-PC, Dasibi Environmental Co., Glendale, CA, USA), two higher-cost personal O_3 monitors (Model POM, 2B Technologies Inc., Boulder, CO, USA), and two lower-cost personal O_3 monitors (Series 500, Aeroqual LLC., Auckland, New Zealand) (see Figure 2a). All O_3 monitoring instruments were adjusted to report the O_3 concentration at 5 min intervals. Depending on the target concentration value, the time to reach the target concentration in the chamber from the baseline and the time to return to the

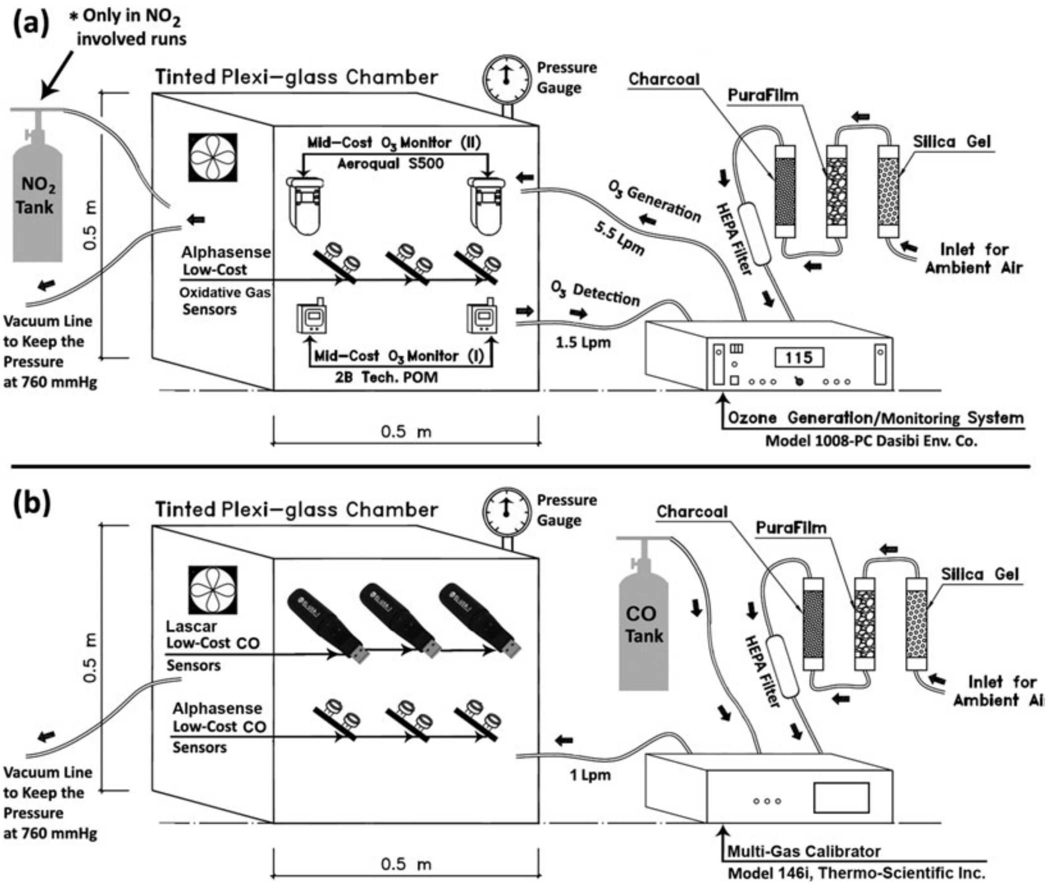

Figure 2. Schematic of the experimental set-up: (a) evaluation of the oxidative gas sensors and (b) evaluation of the CO sensors.

baseline concentration from the target concentration was 30–60 min.

Specification of the O_3 and NO_2 monitoring instruments are summarized in Table 1. The O_3 analyzers manufactured by Dasibi Environmental Co. and 2B Technologies Inc. both operate on the principle of ultraviolet (UV) absorption. Designated as a reference method by the USEPA, the UV absorption mechanism is an accurate and well characterized method employing a mercury lamp that emits light primarily of wavelength 254 nm, which corresponds to the maximally absorbed wavelength of O_3.[25] The reference ozone-free air flow for O_3 detection is generated using an ozone-specific scrubber on a substrate inside the instruments. The personal O_3 monitor manufactured by Aeroqual LLC. utilizes a semi-conductor oxide O_3 sensor (OZU 0-0.15 ppm), and has been used commonly for O_3 detection in air quality monitoring networks.[26–28] The operating principle of the Aeroqual S500 includes drawing sample air into an enclosure wherein the oxidizing capacity of the ozone molecules modifies the electrical state of a heated thin film of tungsten oxide as the sensing material.[26] Since the electrical conductivity of the material is a strong function of the temperature and RH, devices operating

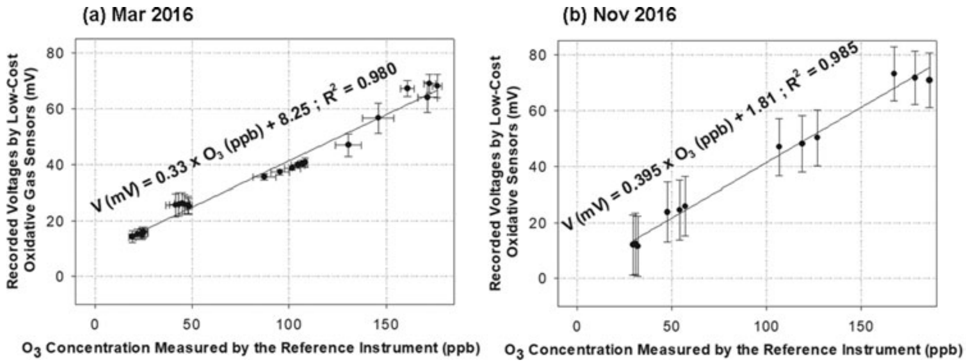

Figure 3. Recorded voltages by the electro-chemical oxidative gas sensors at different target O_3 concentrations (error bars indicate standard errors): (a) results of the experiments performed in Mar 2016 with a newly opened sensor and (b) results of the experiments performed on the same sensors in Nov 2016.

Table 1. Specification of the O_3 and NO_2 monitoring instruments used in the study.

Manufacturer	Detecting Gas	Detection Mechanism	Measuring Range	Resolution	Approximate Cost (US $)
Model 1008-PC, Dasibi Environmental Co., Glendale, CA, USA	O_3	UV absorption	0 – 1000 ppb	±1 ppb	> 20,000
Model POM, 2B Technologies Inc., Boulder, CO, USA	O_3	UV absorption	3 – 10000 ppb	±0.1 ppb	5000
Series 500, Aeroqual LLC, Auckland, New Zealand	O_3	Semi-conduction oxidizing	0 – 150 ppb	±1 ppb	1000
RM Series, Interscan Co., Simi Valley, CA, USA	NO_2	Liquid sorbent	0 – 2 ppm	±0.1 ppm	> 5,000
Alphasense Co., Essex, UK	O_3 or NO_2	Electro-chemical	Analog output of 0 – 5 V	±0.01 mV	100

based on this semi-conduction oxidizing mechanism are not a reference method for the detection of O_3.

Exposure to NO_2 was performed separately by introduction of compressed NO_2 into the chamber, after dilution with zero air, using a dynamic gas calibrator (Model 146i, Thermo Fisher-Scientific Inc., Franklin, MA, USA). A bench-top liquid sorbent NO_2 analyzer (RM Series, Interscan Co., Simi Valley, CA, USA) was used for measurement of the NO_2 inside the chamber (see Figure 2a). Although analysis by chemiluminescence is considered the most reliable and preferred method for NO_2 detection, the liquid sorbent-based NO_2 analyzers (e.g., Interscan NO_2 analyzer, used in this study) have demonstrated a high NO_2 measurement accuracy when used in the laboratory (less than 5% bias compared to the chemiluminescence method for NO_2 concentrations below 5 ppm).[29] The NO_2 monitor was factory-calibrated before the first experiment, and was zeroed and re-calibrated with zero air before each experiment. Tested target concentrations of NO_2 included 0.2, 0.5, 1, and 1.5 ppm, which are common NO_2 concentrations in urban areas.[30]

Performance of sensors was evaluated by estimating accuracy and linearity of the sensors compared to the reference instruments. As formulated in Equation (1), the bias (B) as a measure for accuracy of the sensors was quantified as the average ratio of the difference between concentration values estimated by the Alphasense sensor ($C_{\text{Alphasense}}$, using derived regression lines) and that by the reference instruments (C_{Actual}) to the C_{Actual} for each measurement during the steady-state period of the experiment. As a measure of intra-unit variability of the sensors, the coefficient of variation (CV) of the sensors was calculated using Equation (2):

$$B\ (\%) = \frac{1}{n}\sum_{i=1}^{n}\frac{C_{Alphasense,\ i} - C_{Actual,\ i}}{C_{Actual,\ i}} \times 100 \qquad \text{Eq. (1)}$$

$$CV\ (\%) = \frac{1}{n}\sum_{i=1}^{n}\frac{\sigma_i}{\mu_i} \times 100, \qquad \text{Eq. (2)}$$

where σ_i is the standard deviation at concentration i and μ_i is the mean of the measurements at the i^{th} concentration from three replicate sensors for each test. Linearity of the sensors was evaluated by estimating the r-squared as a measure of closeness of the recorded voltages to the fitted regression line for different reference concentrations.

Evaluation of the CO sensors

Specifications for the CO monitoring instruments are summarized in Table 2. The experimental procedure for evaluation of the CO sensors was similar to that of the oxidative gas sensors. The same cycle of ascending, steady state, and descending periods for target concentrations of (2, 5, 10, 12, 15, 25, 30, and 50 ppm) was followed for CO as for O_3 and NO_2. The CO gas was introduced at a controlled and constant concentration into the chamber from a compressed tank after dilution with zero air and adjustment by the gas calibrator. The flow rate provided by the gas calibrator to the chamber varies depending on the selected concentration of the target gas. In this study, the reference measurement of CO concentrations was estimated using an electro-chemical portable probe developed by (GrayWolf

Table 2. Specification of the CO monitoring instruments used in the study.

Manufacturer	Detection Mechanism	Concentration Range	Resolution	Approximate Cost (US $)
GrayWolf Advanced Pro, GrayWolf Sensing Solutions LLC, Shelton, CT, USA	Electro-chemical	0–500 ppm	± 0.1 ppm	> 15,000
Model EL-USB-CO Lascar Electronics Inc., Essex, UK	Electro-chemical	3–1000 ppm	± 7 ppm	200
Alphasense Co., Essex, UK	Electro-chemical	Analog output of 0 – 5 V	± 0.01 mV	100

Advanced Pro, GrayWolf Sensing Solutions LLC., Shelton, CT, USA). Reliability verification of this reference electrochemical monitor along with detailed discussion on comparison to EPA reference methods have been reported in literature.[31,32] Prior to measurements, the instrument was factory-calibrated to measure CO concentrations between 0–100 ppm with a precision of ±0.2 ppm. Each Alphasense sensor was co-located with a commercially available CO sensor (EL-USB-CO, Lascar Electronics Inc., Essex, UK) to compare the recorded voltages by the Alphasense sensor with respect to another electrochemical sensor (see Figure 2b). The same performance metrics as for the oxidative gas sensors were estimated for the CO sensors.

Evaluation of the response times

Response time is the time required for a sensor to reach a certain percentage of the steady-state value. We evaluated the response time of the sensors to identify their ability to capture transient peaks in exposure and to determine the needed time when bump-checking these sensors in the field with calibration gases. The response time of three sensors of each type was reported as t_{50} and t_{90} values, defined as the time required for the sensor voltage to reach 50% and 90% of the steady-state reading for the span tests (15 ppm CO for CO sensors or 2 ppm NO_2 for oxidative gas sensors). The reason for using NO_2-only to evaluate the response time of the oxidative gas sensors was availability of compressed NO_2 cylinders on the market. For this purpose, a factory-fabricated shroud was used. The shroud had a single entry and supplied the gas directly from the tank to each sensor, one at a time. The zero and span gas tests were performed on each of the CO and oxidative gas sensors, separately. Two exposure flow rates of 0.25 Lpm (Test A) and the manufacturer recommended 0.5 Lpm (Test B) were regulated through the shroud. The response time estimated in this study is based on direct injection of zero air or span gases into the sensor head. This response time is required for obtaining insight into the field calibration protocol.

Results and discussion

Evaluation of the oxidative gas sensors

Recorded voltages corresponding to the target concentrations indicated a highly linear relationship with ozone (see Figure 3a). The change in the relationship after nine months of continuous operation is also displayed in Figure 3b. Although the electro-chemical sensors maintained the linear association with O_3 concentrations measured inside the chamber (with almost the same R^2 of 0.98), there was an increase in the line slope from 0.330 to 0.395 (about 20%) and a reduction in the intercept as an aging influence. The mean change in the recorded voltages agreed with the drift reported by the manufacturer (2% drift in recorded values per month). We also observed an increase in intra-sensor variability after the 9-month period. The average size of the error bars at different concentrations was ± 22 mV, which was about 2–7 times greater than the variability observed when the sensors were new. This suggests the sensors not only drift, but also become less precise over time or the sensors may not drift equally over time. The manufacturer suggested lifetime for Alphasense oxidative gas sensors is 24 months, when the sensors experience a 50% change in their reading as compared to the first day of operation.

The time series of O_3 concentrations measured by high- and mid-cost instruments listed in Table 1 (reference instrument and two types of personal O_3 monitors) were compared to the low-cost sensors, as displayed in Figure 4. The concentrations associated with the oxidative gas sensors were estimated using the equation obtained from the regression analysis when relating the steady-state target concentration to the recorded voltages (Figure 3a). Although the three Alphasense sensors overestimated the concentration in the beginning of the test when O_3 concentrations were close to the background (< 10 ppb), they were more consistent with the reference instrument for concentrations above 25 ppb. The fact that the POM monitor and the reference instrument operate on the same detection principle is probably the reason for obtaining similar O_3 concentrations by them throughout the measurement periods. However, the POM monitors overestimated the concentration when the targeted concentration was relatively high (100 or 150 ppb, as seen in Figures 4c and 4d). In contrast, the Aeroqual monitors consistently underestimated the O_3 concentration, which was more obvious at higher concentrations. O_3 monitors using semi-conduction oxidizing mechanism are sensitive to environmental conditions, particularly temperature and RH.[33] The temperature inside our chamber increased by 5°C (starting at ~25°C and ending at ~30°C) and the RH decreased by 20% (starting at about 65% and ending at 45%) over the course of the experiment. These changes in temperature and relative humidity might contribute to underestimation of the real concentrations by the Aeroqual monitor and Alphasense sensors.

The voltages recorded by the Alphasense oxidative gas sensor were strongly linear ($R^2 = 0.996$) at steady-state NO_2 concentrations (Figure 5). Interestingly, the slope of the regression line for NO_2 (0.37) was similar to that for O_3 (0.33). This finding indicates that the oxidative gas sensors are almost equally sensitive to O_3 and NO_2, when exposed separately (see Figure 5). Since both selected

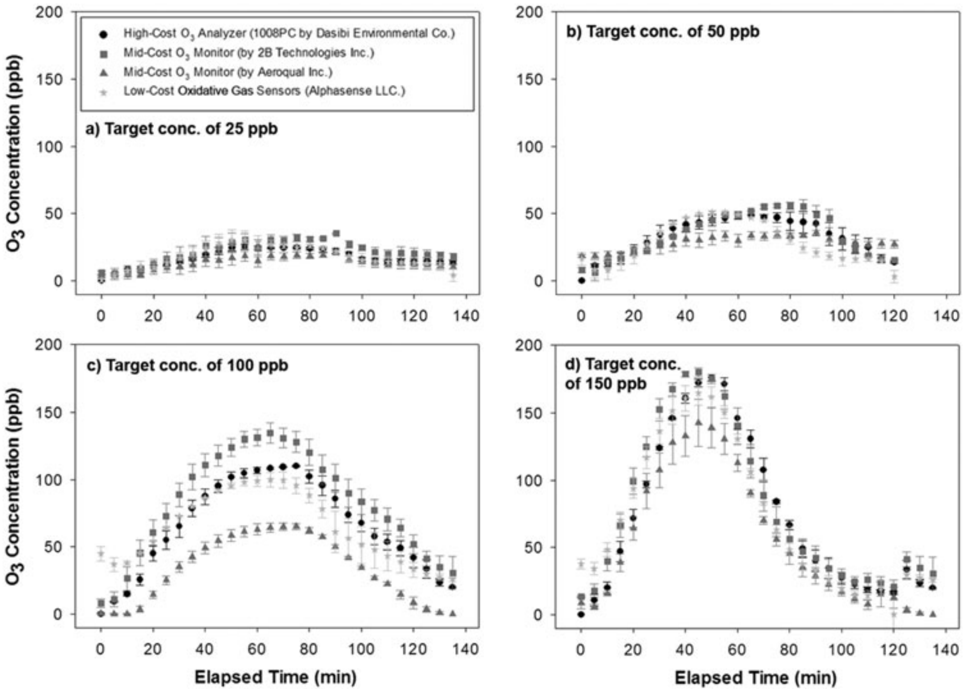

Figure 4. Time series of O_3 concentrations measured by different O_3 monitors in comparison to predicted O_3 concentration values according to the recorded voltages by the Alphasense oxidative gas sensors (error bars indicate standard errors): (a) target concentration of 25 ppb; (b) target concentration of 50 ppb; (c) target concentration of 100 ppb; and (d) target concentration of 150 ppb.

ranges of concentrations for O_3-only and NO_2-only included the range commonly measured in the ambient air, the oxidative gas sensors are recommended for use in situations where only O_3 or NO_2 are present, or when knowledge of the combined concentration is acceptable, as it is not possible to distinguish between O_3 and NO_2.

Each oxidative gas sensor is provided with a slope and an intercept specified by the manufacturer. According to the manufacturer, the mean slope and intercept for O_3 of the three oxidative gas sensors tested in this study were 0.318 mV/ppb and 208 mV, respectively. The equivalent values for the sensors when exposed to O_3 in our test conditions were 0.33 mV/ppb and 8.25 mV (Figure 5). Thus, the estimated slopes for O_3 from this study was fairly similar compared to those provided by the manufacturer. However, due to the considerable difference between the intercept reported by the manufacturer and that determined in this study, direct application of the manufacturer's calibration line for estimation of the environmental O_3 concentration using Alphasense oxidative gas sensor is cautioned.

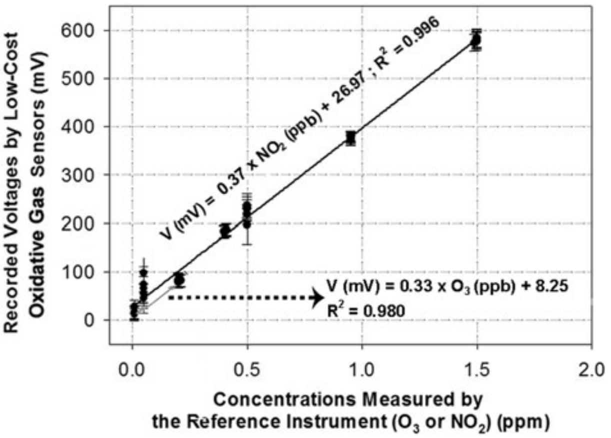

Figure 5. Recorded voltages by the Alphasense oxidative gas sensors at different target NO_2 concentrations (error bars indicate standard errors).

The bias and CV of the Alphasense oxidative gas sensors relative to reference analyzer (by Dasibi Environmental Co.) for different target concentrations were summarized in Table 3. All sensors/monitors showed a lower accuracy at the lowest target concentration (25 ppb of O_3 or 0.2 ppm of NO_2). The Alphasense sensors were less accurate in environments with low (25 ppb) or high (150 ppb) O_3 concentrations. Both the bias and CV values for cases at 50 and 100 ppb concentrations were below 10%. The Alphasense sensors showed better accuracy for NO_2 exposures. The Aeroqual monitors exhibited the least accuracy among the O_3 sensors (bias values ranging from -27 to -40.6%) and the highest intra-sensor variability (CV values ranging from 6.9–24.6%). The Aeroqual monitors underestimated the target concentration in all cases. As expected, the mid-cost O_3 monitors manufactured by 2B Technologies Inc. demonstrated the best performance among all monitors (bias values ranging from -3.9 to 7.7%). The intra-unit variability of the 2B Tech monitors was higher when the O_3 concentration was

Table 3. Accuracy of measurements by different low-cost O_3/NO_2 sensors and monitors compared to the reference values.

Sensor/Monitor	Bias (%)	CV (%)
Low-cost oxidative gas sensor (by Alphasense LLC)		
Target O_3 concentration of 25 ppb	10.3	17.4
Target O_3 concentration of 50 ppb	3.3	6.1
Target O_3 concentration of 100 ppb	−9.4	7.3
Target O_3 concentration of 150 ppb	−19.4	5.8
Target NO_2 concentration of 0.2 ppm	−24.0	18.2
Target NO_2 concentration of 0.5 ppm	4.7	11.5
Target NO_2 concentration of 1.0 ppm	−2.8	4.9
Target NO_2 concentration of 1.5 ppm	−1.2	4.6
Mid-cost O_3 monitor (by 2B Technologies Inc.)		
Target O_3 concentration of 25 ppb	7.7	18.2
Target O_3 concentration of 50 ppb	3.4	4.4
Target O_3 concentration of 100 ppb	7.1	8.2
Target O_3 concentration of 150 ppb	−3.9	17.4
Mid-cost O_3 monitor (by Aeroqual Inc.)		
Target O_3 concentration of 25 ppb	−27.0	24.6
Target O_3 concentration of 50 ppb	−32.0	13.2
Target O_3 concentration of 100 ppb	−40.6	6.9
Target O_3 concentration of 150 ppb	−29.5	11.3

the lowest (25 ppb) or the highest (150 ppb) and lower for intermediate concentrations. These monitors overestimated the concentration for target O_3 concentrations below 100 ppb. In general, bias and CV values obtained from Alphasense oxidative gas sensors were more accurate than the Aeroqual monitors but less accurate than the one by 2B Technologies (except for target concentration of 50 ppb). Except for NO_2 concentration of 0.2 ppm, the CV values for tested NO_2 concentrations were within the 10% acceptance CV value by the EPA for test instruments.

Evaluation of the CO sensors

We observed a strong linear relationship ($R^2 > 0.998$) between voltages from the Alphasense CO sensors and the reference instrument for CO concentrations below 12 ppm (Figure 6). There were negligible increases in the voltage (from 4.5 to 4.8 mV) recorded by the Alphasense CO sensors when the target concentration increased over a wide CO concentration ranging from 12–50 ppm. Thus, these sensors are inappropriate for use in environments with CO concentrations above 12 ppm. Using the linear relationship between the Alphasense sensors and the reference instrument, the CO concentration values for voltages recorded by the Alphasense sensors at different target concentrations were calculated and plotted against Lascar CO monitors in Figure 7. For all target concentrations less than 12 ppm (Figures 7a–7d), both the Lascar electro-chemical sensors and the Alphasense CO sensors demonstrated a very similar response. However, the Lascar CO sensors overestimated the CO concentrations (up to 10%) when the targeted concentration was 12 ppm. This overestimation by the Lascar sensors was also observed at target concentration above 12 ppm. The Lascar CO sensors showed a wider range of proper CO measurement for target CO concentrations up to 50 ppm. The intra-sensor variability of the measurements by the Lascar sensors for all targeted CO concentrations was greater than the Alphasense CO sensors. Considering the lower cost of the Alphasense sensors (about half of the Lascar sensors cost) yielding similar set of the results, the Alphasense sensors may be appropriate for use in an air quality monitoring network where concentrations generally below 12 ppm are expected.

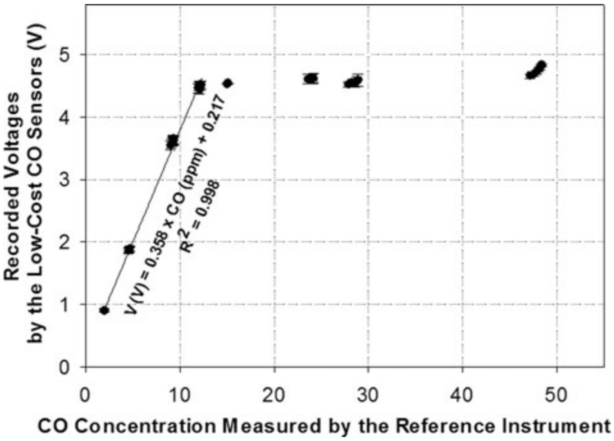

Figure 6. Recorded voltages by the Alphasense CO sensors at different target CO concentrations (error bars indicate standard errors which may be smaller than the symbol size).

Compared to the oxidative gas sensors, the Alphasense CO sensors revealed much lower bias and CV values over its measurement range of 2–12 ppm. In fact, all biases were below 10% in all tested target CO concentrations (2.2–5.9%, as listed in Table 4). CV as a measure for the mean intra-unit variability was consistently below 5%. The Lascar CO sensors showed a poor accuracy for CO

Table 4. Accuracy of measurements by different low-cost CO sensors and monitors compared to the reference values.

Sensor/Monitor	Bias (%)	CV (%)
Low-cost oxidative gas sensor (by Alphasense LLC)		
Target concentration of 2 ppm	3.3	3.4
Target concentration of 5 ppm	2.2	3.2
Target concentration of 10 ppm	5.9	2.8
Target concentration of 12 ppm	−5.0	2.2
Mid-cost CO monitor (by Lascar Inc.)		
Target concentration of 2 ppm	22.9	37.8
Target concentration of 5 ppm	21.7	18.4
Target concentration of 10 ppm	6.2	0.4
Target concentration of 12 ppm	−3.5	9.6
Target concentration of 15 ppm	−2.5	7.3
Target concentration of 25 ppm	3.5	9.1
Target concentration of 30 ppm	11.1	6.8
Target concentration of 50 ppm	14.9	2.3

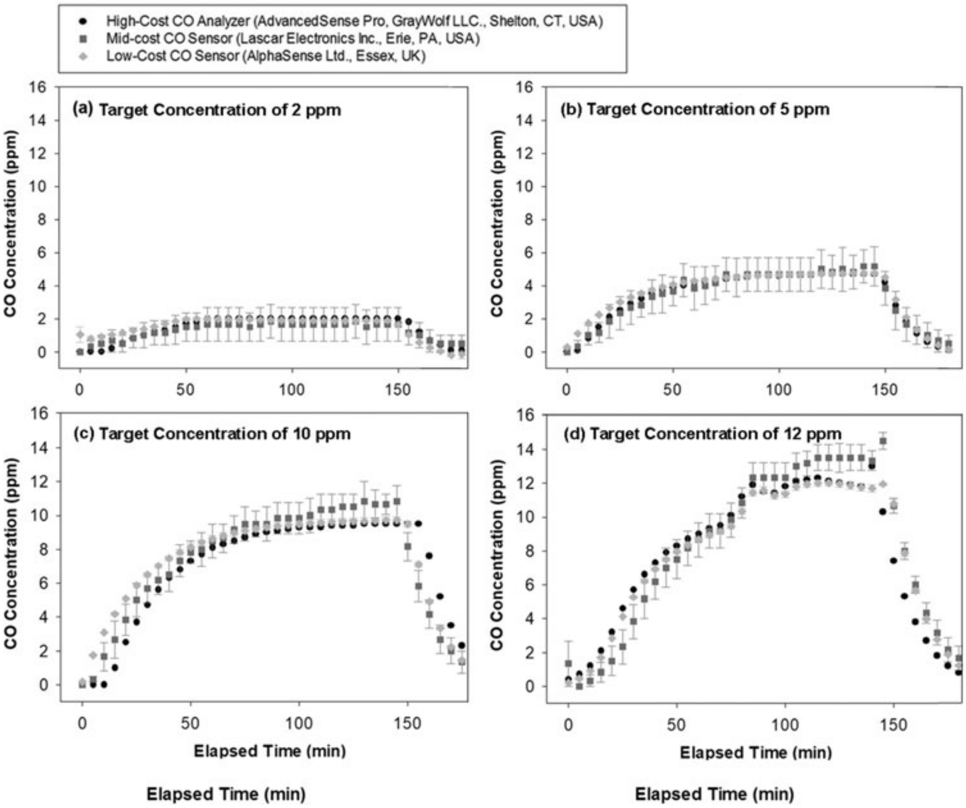

Figure 7. Time series of CO concentrations measured by different CO monitors for different target CO concentrations of (a) 2 ppm, (b) 5 ppm, (c) 10 ppm, (d) 10 ppm, and (d) 12 ppm, (error bars indicate standard errors which may be smaller than the symbol size), where the CO concentrations for the Alphasense sensor are calculated from the linear regression presented in Figure 6.

concentration below 5 ppm (biases above 21%) but they showed a good accuracy over a wider range of CO concentration values (5–25 ppm). These sensors overestimated CO concentrations considerably (bias > +10%) when the target CO concentration exceeded 25 ppm.

In summary, the use of the Alphasense CO sensor, as set up we observed, is not recommended for situations where concentrations above 12 ppm are expected (see Figure 6). However, the maximum daily concentrations of the CO measured in ambient air of seven major cities of the US have been below 5 ppm.[34] In occupational settings, CO concentrations can be considerably higher than 12 ppm. Thus, the use of Alphasense CO sensors are not recommended for occupational monitoring where high concentrations are anticipated.

Evaluation of the response time

The response times, t_{50} and t_{90}, of the oxidative gas and CO sensors for different tests are summarized in Table 5. Except for Test A for span NO_2 concentration of 2 ppm, wherein the response times of t_{90} was not achieved in 600 s, the response time of the sensors decreased with an increase in the flow rate. The voltages from the

Table 5. Response time, (t_{50} and t_{90}, corresponding to 50% and 90%, respectively, of the steady-state reading) expected voltage of the Alphasense oxidative gas and CO sensors for zero and span tests.

Bump test	Target concentration (ppm)	Steady-state reading at 0.25 Lpm (mV)	t_{50} (s) at 0.25 Lpm	t_{90} (s) at 0.25 Lpm	Steady-state reading at 0.50 Lpm (mV)	t_{50} (s) at 0.50 Lpm	t_{90} (s) at 0.50 Lpm
Oxidative gas sensors							
a) Zero air to oxidative gas sensor	0	−20	22	198	−21	20	147
b) 2 ppm NO_2 to oxidative gas sensor	2	553	26	N/A	612	20	48
CO sensors							
c) Zero air to CO sensor	0	−54	284	699	−60	216	623
d) 15 ppm CO to CO sensor	15	4513	20	45	4498	20	44

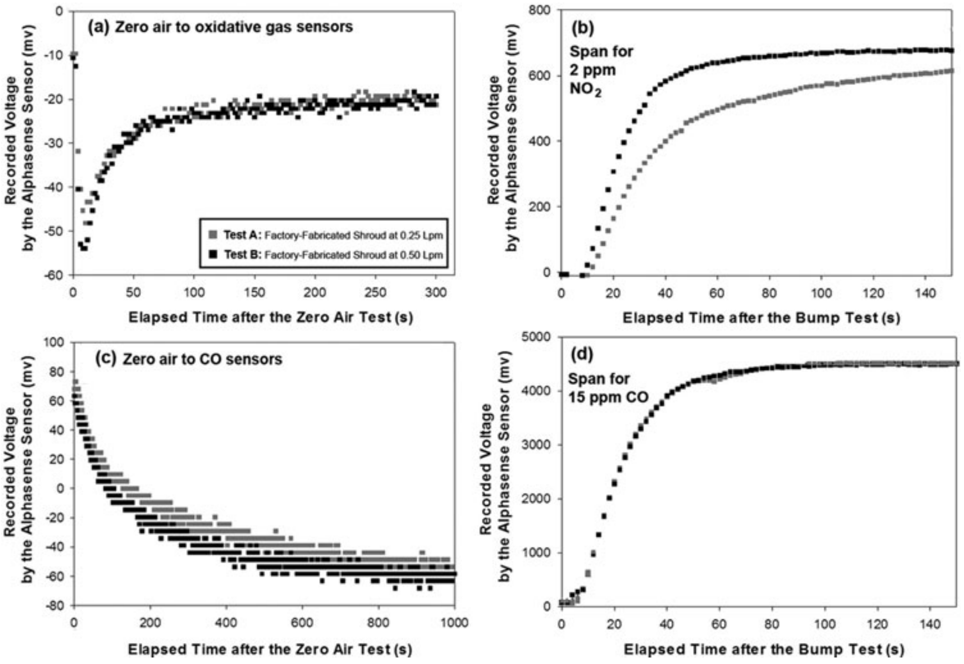

Figure 8. Response time of the Alphasense sensors obtained from the bump test: (a) zero air test of the oxidative gas sensor; (b) span test of the oxidative gas sensor with NO_2 at concentration of 2 ppm; (c) zero air test of CO sensor; and (d) span test of CO sensor with CO at concentration of 15 ppm.

oxidative gas sensors were all negative during the entire zero test period. Since there is no physical meaning for the negative voltage values the electro-chemical oxidative gas sensors at near-zero NO_2 concentrations may not be reliable. Although the behavior of the oxidative gas sensors at different zero air flow rates of 0.25 and 0.5 Lpm were similar (see Figure 8a), the response time of the higher flow rate was shorter (e.g., $t_{90} = 198$ at the flow rate of 0.25 Lpm vs 147 s at the flow rate of 0.5 Lpm). When first exposed to zero air, the voltage dropped rapidly and then slowly approached zero. However, none of the tested cases reached voltages higher than about -15 mV after 300 s. This result presents a challenge when conducting a zero air test on these oxidative gas sensors for field calibration. We speculate that the negative voltages are associated with very low (less than 10%) relative humidity inside the bumping shroud, which rarely occurs in ambient air. In fact, the decrease in relative humidity due to direct exposure to zero air lead to further oxidation of the sensors than during passive exposure to environmental O_3.[35] Thus, the recorded voltages showed a drift toward negative values. For the span test at the flow rate of 0.5 Lpm, saturation of the oxidative gas sensors with the span gas (2 ppm NO_2) was achieved faster ($t_{50} = 20$ and $t_{90} = 48$ s) than the span test at the flow rate of 0.25 Lpm, which could not reach the steady state during the entire test time (150 sec), as seen in Figure 8b.

Similar to the oxidative gas sensors, all recorded voltages were negative after 80 s of zero air exposure, likely due to the decrease in RH. The CO sensors required a longer time than the oxidative gas sensors to report a steady voltage (about -60 mV, as displayed in Figure 8c). In contrast to the oxidative gas sensors, there were shorter response times for the span test of the CO sensors at both tested flow rates compared to the oxidative gas sensors. The flow rate had a negligible effect on the response time (t_{90} of 45 vs. t_{90} of 44 s) at the span concentration of 15 ppm of CO (Figure 8d). In conclusion, the higher flow rate, 0.5 Lpm recommended by the manufacturer, is suggested only for field calibration of the oxidative gas sensors. A lower flow rate (e.g., 0.25 Lpm) is recommended for field calibration of the CO sensors as it will require less gas. No flow rates higher than 0.5 Lpm were tested in this study, as it was not recommended by the manufacturer.

Conclusions

We evaluated low-cost electro-chemical sensors from Alphasense Ltd. for real-time monitoring of CO, NO_2, and O_3 gases. Sensor response voltages were found to be highly linear to gas concentrations measured with reference instruments for environmental O_3 concentrations between 25–150 ppb, NO_2 concentrations between 0.2–1.5 ppm and CO concentrations below 12 ppm. Since the CO sensors were found to be reliable only at environmental concentrations below 12 ppm, its application may be limited to certain industries and ambient air stations where high CO concentrations are expected. The oxidative gas sensors were sensitive to both O_3 and NO_2, and recorded similar voltages for the common ranges of O_3 or NO_2 concentrations (25–150 ppb for O_3 and 0.2–1.5 ppm for NO_2).

The bump tests exposing the sensors to zero air and span concentrations revealed that the CO sensors were not sensitive to flow rate of the calibrating gas. However, the zero air at flow rates below 0.5 Lpm led to negative voltage values, which may be due to relative humidity reduction of the calibrating gases. The response time of the oxidative gas sensors, when NO_2 was used for calibration, was strongly dependent on the flow rate. Aging also biased the voltage recording at certain environmental O_3 concentrations (about 20% after 9 months of continuous operation), so frequent calibration of the oxidative gas sensor is highly recommended. Since the biases of these sensors were higher than 10% at high O_3 concentrations ($>$ 100 ppb) and at low NO_2 concentrations ($<$ 0.2 ppm), their applications in low NO_2 and high O_3 environments must be cautioned.

Conflict of interest

The authors disclaim any conflict of interest for the present study.

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References

[1] **Mofarrah, A. and T. Husain**: A holistic approach for optimal design of air quality monitoring network expansion in an urban area. *Atmos. Environ. 44*:432–440 (2010).

[2] **Liu, M.K., J. Avrin, R.I. Pllack, J.V. Behar, and J.L. McElroy**: Methodology for designing air quality monitoring networks: I. Theoretical aspects. *Environ. Monit. Assess. 6*:1–11 (1986).

[3] **USEPA**: Criteria Air Pollutants. Available at https://www.epa.gov/criteria-air-pollutants.

[4] **Ran, L., C. Zhao, F. Geng, X. Tie, X. Tang, L. Peng, et al.**: Ozone photochemical production in urban Shanghai, China: Analysis based on ground level observations. *J. Geophys. Res. Atmos. 114*(D15) (2009).

[5] **Godish, T., W.T. Davis, and J.S. Fu**: *Air Quality*. Boca Raton: CRC Press, 2014.

[6] **Bornholdt J., Dybdahl, U. Vogel, M. Hansen, S. Loft, and H. Wallin**: Inhalation of ozone induces DNA strand breaks and inflammation in mice. Mutation Research/Genetic. *Toxicol. Environ. Mutag. 520*:63–72 (2002).

[7] **Liu, H., Y. Wu, and H. Chen**: Production of ozone and reactive oxygen species after welding. *Arch. Environ. Contam. Toxicol. 53*:513–518 (2007).

[8] **Lippmann, M.**: Health effects of ozone. A critical review. *JAPCA* 39:672–695 (1989).

[9] **Finlayson-Pitts, B. J. and J.N. Pitts**, *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*. San Diego: Academic Press, (1999).

[10] **OSHA**: Table Z-1 Limits for Air Contaminants, Available at https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=standards&p_id=9992

[11] **Olivier, J.G.J., A.F. Bouwman, K.W. Van der Hoek, and J.J.M. Berdowski**: Global air emission inventories for anthropogenic sources of NO_x, NH_3 and N_2O in 1990. *Environ. Pollut. 102*:135–148 (1998).

[12] **Kampa, M., and E. Castanas:** Human health effects of air pollution. *Environ. Pollut. 151*:362–367 (2008).

[13] **Barnard, R.J., and J.S. Weber**: Carbon monoxide: A hazard to fire fighters. *Arch. Environ. Health. 34*:255–257 (1979).

[14] **Raub, J.A., M. Mathieu-Nolf, N.B. Hampson, and S.R. Thom**: Carbon monoxide poisoning—A public health perspective. *Toxicol. 145*:1–14 (2000).

[15] **Klaratna, N., and B.H. Sudantha**: An environmental air pollution monitoring system based on the IEEE 1451 standard for low cost requirements. *IEEE Sensors J. 8*:415–422 (2008).

[16] **Shindo, J., K. Oi, and Y. Matsumoto**: Considerations on air pollution monitoring network design in the light of spatio-temporal variations of data. *Atmos. Environ. Part B. Urb. Atmosph. 24*:335–342 (1990).

[17] **Vedal, S., M. Brauer, R. White, and J. Petkau**: Air pollution and daily mortality in a city with low levels of pollution. *Environ. Health Perspec. 111*:45–51 (2003).

[18] **Khedo, K.K., R. Perseedoss, and A. Mungur**: A wireless sensor network air pollution monitoring system. arXiv preprint arXiv:1005.1737 (2010).

[19] **Postolache, O.A., J.D. Pereira, and P.S. Girao**: Smart sensors network for air quality monitoring applications. *IEEE Trans. Instrument. Measure. 58*:3253–3262 (2009).

[20] **Wang, D., D.P. Agrawal, W. Toruksa, C. Chaiwatpongsakorn, M. Lu, and T.C. Keener**: Monitoring ambient air quality with carbon monoxide sensor-based wireless network. *Communications of the ACM. 53*:138–1141 (2010).

[21] **Honicky, R. J. E. Brewer, E. Paulos, and R. White**: N-smarts: networked suite of mobile atmospheric real-time sensors. In Proceedings of the Second ACM SIGCOMM Workshop on Networked Systems for Developing Regions. *ACM* (2008).

[22] **Meixner, H., and U. Lampe**: Metal oxide sensors. *Sensor Actuat B-Chem. 33*:198–202 (1996).

[23] **Mead, M.I., O.A.M. Popoola, G.B. Stewart, P. Landshoff, M. Calleja, M. Hayes, et al.**: The use of electrochemical sensors for monitoring urban air quality in

low-cost, high density networks. *Atmos. Environ. 70*:186–203 (2013).

[24] **Pires, J.C.M., S.I.V. Sousa, M.C. Pereira, M.C.M. Alvim-Ferraz, and F.G. Martins**: Management of air quality monitoring using principal component and cluster analysis-part II: CO, NO_2 and O_3. *Atmos. Environ. 42*:1261–1274 (2008).

[25] **Williams E.J., F.C. Fehsenfeld, B.T. Jobson, W.C. Kuster, P.D. Goldan, J. Stutz, and W.A. McClenny**: Comparison of ultraviolet absorbance, chemiluminescence and DOAS instruments for ambient ozone monitoring. *Environ. Sci. Technol. 40*:5755–5762 (2006).

[26] **Kanda, I.**: Measurement of ozone concentration on the elevation gradient of a low hill by a semiconductor-based portable monitor. *Atmosphere 6*:928–941 (2015).

[27] **Selvaraj, R.S., K. Elampari, R. Gayathri, and S.J. Jeyakumar**: A neural network model for short term prediction of surface ozone at tropical city. *Int. J. Eng. Sci. Tech. 2*:5306–5312 (2010).

[28] **Hamdun, A., and T. Arakaki**: Analysis of ground level ozone and nitrogen oxides in the city of Dar es Salaam and the rural area of Bagamoyo, Tanzania. *J. Air Pol. 4*:224–238 (2015).

[29] **Laitinen, J., J. Liesivuori, M. Linnainmaa, and P. Kalliokoski**: Evaluation of monitoring methods for nitrogen oxides. *Ann. Occup. Hyg. 37*:307–314 (1993).

[30] **Cyrys, J., M. Eeftens, J. Heinrich, C. Ampe, A. Armengaud, R. Beelen, et al.**: Variation of NO_2 and NO_x concentrations between and within 36 European study areas: Results from the ESCAPE study. *Atmos. Environ. 62*:374–390 (2012).

[31] **Andress, J., B.S. McCall, R.A. Overfelt, J.W. Fergus, B.C. Prorok, M.S. Crumpler, and L.C. Mathison**: Overview of commercial electrochemical carbon monoxide sensors for aircraft applications. *42nd International Conference on Environmental Systems*, AIAA, pp. 2012–3442 (2012).

[32] **Klitzman, S., J. Caravanos, D. Deitcher, L. Rothenberg, C. Belanoff, R. Kramer, and L. Cohen**: Prevalence and predictors of residential health hazards: A pilot study. *J. Occupa. Environ. Hyg. 2*:293–301 (2005).

[33] **Korotcenkov, G.**: Metal oxides for solid-state gas sensors: What determines our choice? *Mat. Sci. Eng.*: *B. 139*:1–23 (2007).

[34] **Morris, R.D., E.N., Naumova, and R.L. Munasinghe**: Ambient air pollution and hospitalization for congestive heart failure among elderly people in seven large US cities. *Am. J. Publ. Health 85*:1361–365 (1995).

[35] **James, D., S.M., Scott, Z., Ali, and W.T. O'Hare**: Chemical sensors for electronic nose systems. *Microchim. Acta. 149*:1–17 (2005).