

# Absolute and Relative Gas Concentration: Understanding Oxygen in Air

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## Absolute and Relative Gas Concentration

Gas concentration is described in two ways, absolute and relative concentration (Table 1). The ideal gas law yields absolute gas concentration [ $\text{mol m}^{-3}$ ]:

$$PV = nRT \quad (1)$$

where  $P$  is pressure [Pa],  $V$  is volume [ $\text{m}^3$ ],  $n$  is gas quantity [mol],  $T$  is temperature [K],  $R$  is the ideal gas constant ( $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and rearranging Eq. (1) to solve for  $n / V$  [ $\text{mol m}^{-3}$ ] yields absolute gas concentration (Table 1). However, the simplest and most common way to report the concentration of a specific gas in a mixture is by expressing it relative to the other gases in the mixture, as a fraction or percentage (Table 1). For example, the amount of oxygen ( $\text{O}_2$ ) in the atmosphere, assuming there is no water vapor in the atmosphere, is 0.2095 kPa  $\text{O}_2$  per kPa air or 20.95 %. The atmospheric concentration of  $\text{O}_2$  has remained constant for several hundred years at 20.95 %. The percentage is the same at sea level or on Mount Everest. However, the absolute  $\text{O}_2$  concentration does not remain constant. An  $\text{O}_2$  tank is required to climb Mount Everest, even though the relative  $\text{O}_2$  concentration is still 20.95 % (Fig. 1A). The absolute  $\text{O}_2$  concentration determines the rate of most biological and chemical processes, but the relative  $\text{O}_2$  concentration is typically reported. This is analogous to discussing relative humidity when absolute humidity is what determines evaporation rates. Absolute and relative gas concentration measurements can be expressed using several different units (Table 1).

**Table 1. Units used to describe absolute and relative gas concentration measurements.**

<b>Absolute Amount of Gas</b>	<b>Relative Amount of Gas</b>
<b>moles of <math>\text{O}_2</math> per unit volume</b> (e.g. moles per Liter)	<b>% <math>\text{O}_2</math> in air</b> (e.g. 20.95 % in ambient air)
<b>mass of <math>\text{O}_2</math> per unit volume</b> (e.g. grams per Liter; $\text{O}_2$ has a mass of 32 g per mole)	<b>mole fraction</b> (e.g. moles of $\text{O}_2$ per mole of air; 0.2095 mol $\text{O}_2$ per mole of ambient air; this can also be expressed as 0.2095 kPa $\text{O}_2$ per kPa air)
<b>partial pressure</b> (e.g. kilopascals [kPa])	

## Effect of Barometric Pressure on Gas Concentration

The ideal gas law (Eq. (1)) shows that absolute gas concentration increases by 0.987 % at sea level for every 1 kPa increase in pressure ( $1 \text{ kPa} / 101.325 \text{ kPa} = 0.00987$ ). For a sensor that measures absolute gas concentration but is calibrated to read out in relative units, a 1 kPa pressure increase at sea level results in an apparent  $\text{O}_2$  increase of 0.207 % ( $0.00987 * 20.95 \% =$

0.207 %) and an apparent relative O<sub>2</sub> concentration of 21.157 %. The relative gas concentration didn't really increase, but the absolute concentration, which is what sensors measure, did change. This shows up as an apparent change in relative concentration.

Due to lower barometric pressure at higher elevations (Fig. 1A), the percentage increase in absolute gas concentration per kPa increases with elevation. For example, at an elevation of 1358 m (Logan, Utah), the barometric pressure is approximately 86 kPa and the absolute gas concentration increases by 1.16 % for every 1 kPa increase in pressure (1 kPa / 86.0 kPa = 0.0116). Again, for a sensor that measures absolute gas concentration but is calibrated to read out in relative units, this results in an apparent O<sub>2</sub> increase. In this example, 0.247 % O<sub>2</sub> for every 1 kPa increase in barometric pressure (0.0118 \* 20.95 % = 0.243 %) and an apparent relative O<sub>2</sub> concentration of 21.193 %.

A barometric pressure correction should be applied to all O<sub>2</sub> sensors that are calibrated to read relative O<sub>2</sub> concentration. The equation to correct O<sub>2</sub> measurements for barometric pressure at any elevation is:

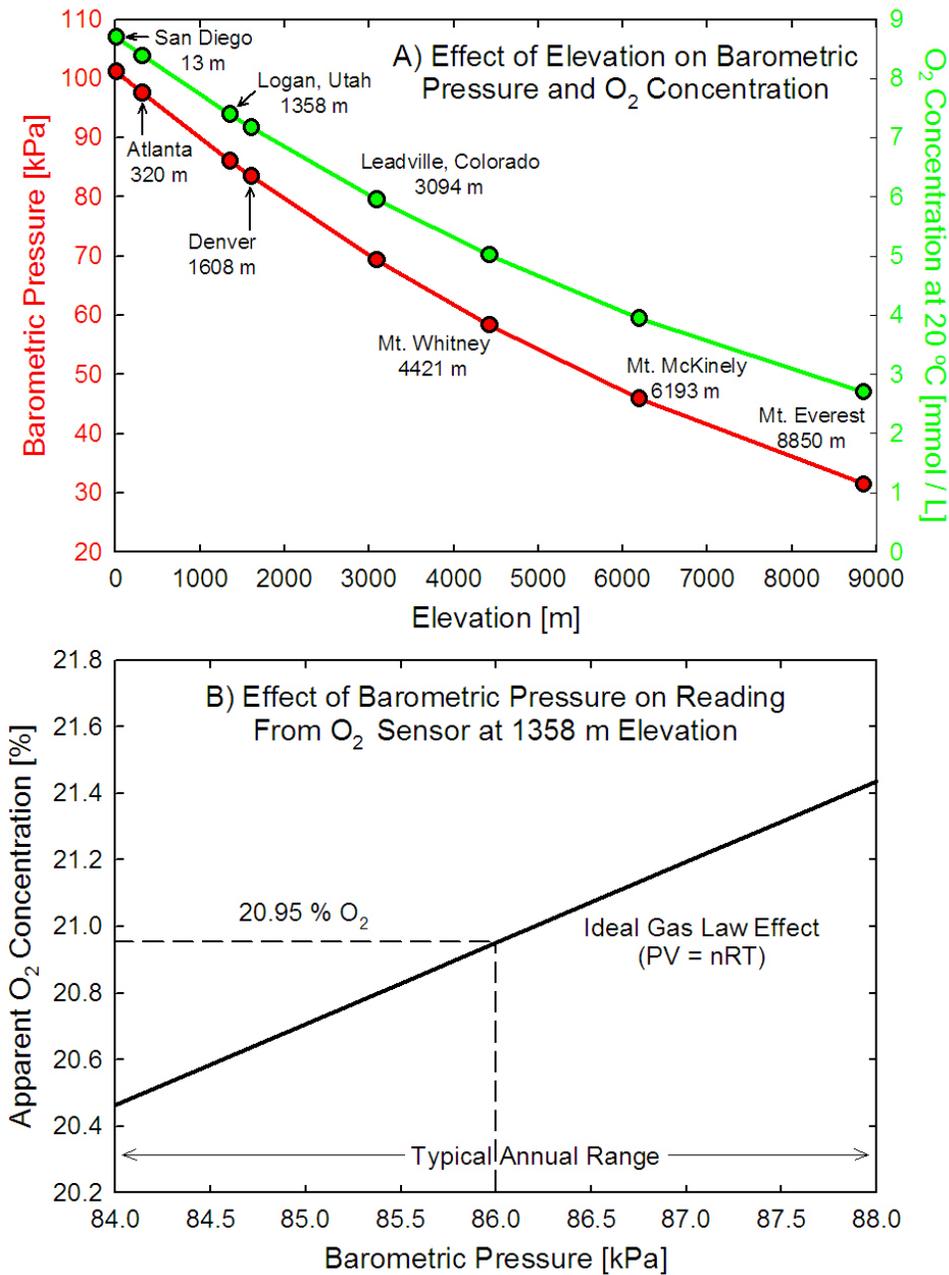
$$O_2 = O_{2M} \left[ 1 - \left( \frac{BP_M - BP_C}{BP_C} \right) \right] \quad (2)$$

where  $O_{2M}$  is measured O<sub>2</sub> concentration [%] (the apparent O<sub>2</sub> concentration),  $BP_C$  is barometric pressure [kPa] at the time of calibration, and  $BP_M$  is barometric pressure [kPa] at the time of the measurement. Approximate barometric pressure for a given elevation is calculated from:

$$BP_{AVE} = 101.325 - 101.325 \left[ 1 - \left( 1 - \frac{E}{44307.69231} \right)^{5.25328} \right] \quad (3)$$

where  $E$  is elevation [m]. In order to make a barometric pressure correction on gas measurements, it must be continuously measured as it changes over time. The typical annual range is approximately 4 kPa, or the average pressure for a given elevation +/- 2 kPa.

The apparent effects of barometric pressure on relative O<sub>2</sub> measurements, based on calculations from Eq. (2), are plotted for 1358 m elevation (Fig. 1B) to show the significance of measuring and correcting for barometric pressure. If not accounted for, barometric pressure fluctuations show up in the O<sub>2</sub> measurement as a change in relative O<sub>2</sub> concentration because sensors respond to absolute O<sub>2</sub> concentration, but are generally calibrated to read relative O<sub>2</sub> concentration.



**Figure 1:** A) Barometric pressure and absolute O<sub>2</sub> concentration [mmol / L] at 20 °C as a function of elevation. Equation (3) was used to calculate barometric pressure. B) The effect of barometric pressure on apparent relative O<sub>2</sub> concentration (O<sub>2</sub> concentration measured with an O<sub>2</sub> sensor). O<sub>2</sub> sensors respond to absolute O<sub>2</sub> concentration but are generally calibrated to yield relative O<sub>2</sub> concentration. As the barometric pressure fluctuates, the absolute O<sub>2</sub> concentration, and thus the O<sub>2</sub> sensor output, fluctuates with it, producing an apparent change in the relative O<sub>2</sub> concentration if the pressure effect is not accounted for. It is assumed the sensor was calibrated at 86.0 kPa. The solid line shows how the apparent relative O<sub>2</sub> concentration is dependent on barometric pressure.

## Effect of Temperature on Gas Concentration

The ideal gas law (Eq. (1)) shows that absolute gas concentration decreases by 0.341 % for a 1 °C increase in temperature from 20 °C (1 K / 293 K = 0.00341). For a sensor that measures absolute gas concentration but is calibrated to read out in relative units, a 1 °C temperature increase from 20 °C results in an apparent decrease of 0.0714 % O<sub>2</sub> (0.341 % \* 0.2095 = 0.0714 %) and a relative O<sub>2</sub> concentration of 20.8786 %. As with barometric pressure, to obtain accurate O<sub>2</sub> measurements a correction should be applied to compensate for temperature effects. The equation to correct O<sub>2</sub> measurements in air for temperature effects is:

$$O_2 = O_{2M} \left[ 1 + \left( \frac{T_M - T_C}{T_C} \right) \right] \quad (4)$$

where  $O_{2M}$  is as given above,  $T_C$  is the air temperature [K] at calibration, and  $T_M$  is the air temperature [K] at the time of the measurement. The effects of temperature on relative O<sub>2</sub> measurements, based on calculations from Eq. (4) are plotted (Fig. 2) to show the significance of measuring and correcting for temperature. If not accounted for, temperature fluctuations show up in the measurement as an apparent change in relative O<sub>2</sub> concentration because sensors respond to absolute O<sub>2</sub> concentration but are calibrated to read relative O<sub>2</sub> concentration.

## Sensor Response to Temperature

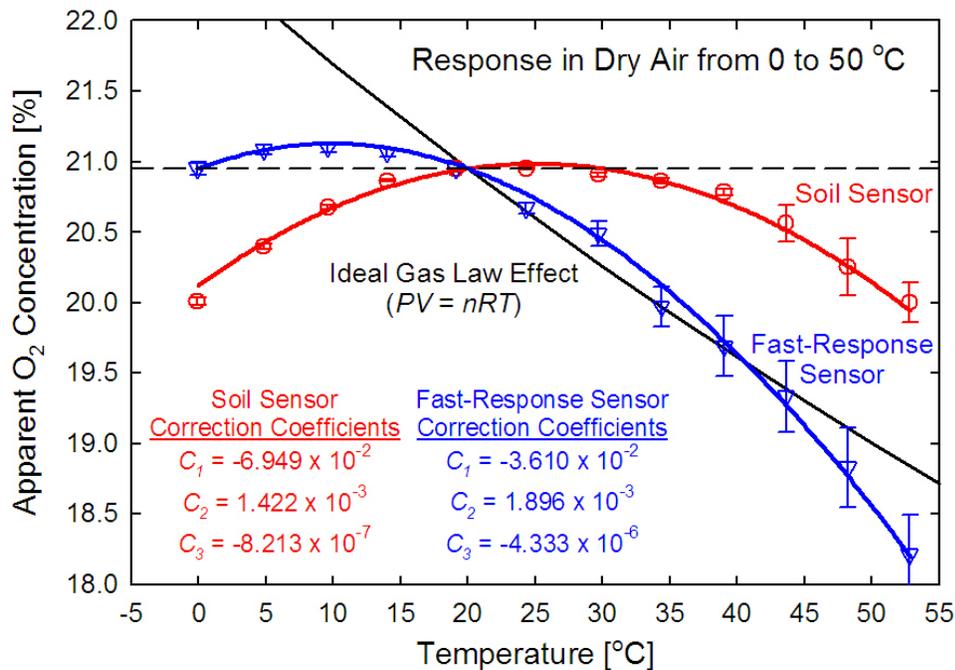
In practice, Eq. (4) does not accurately correct for temperature effects because in addition to the ideal gas law temperature effect, sensor electronics are affected by temperature. The combination of these two effects on Apogee O<sub>2</sub> sensors (soil and fast response sensors) was determined from measurements in dry air across a wide temperature range by plotting pressure-corrected apparent O<sub>2</sub> concentration (i.e., measured O<sub>2</sub> concentration before temperature correction was applied) versus sensor temperature ( $T_S$ ) (Fig. 2). Neither of the sensors follows the ideal gas law response (Fig. 2), and thus an empirical correction derived from the measured data must be applied to account for both the ideal gas law and sensor electronics responses:

$$O_2 = O_{2M} + C_3 T_S^3 + C_2 T_S^2 + C_1 T_S + C_0 \quad (5)$$

where  $T_S$  is the measured sensor temperature [°C] (Apogee O<sub>2</sub> sensors come with a thermistor or type-K thermocouple temperature reference); the coefficients  $C_3$ ,  $C_2$ , and  $C_1$  are listed in Fig. 2 for both the soil and fast-response sensors; and  $C_0$  is the offset coefficient calculated from the temperature at calibration,  $T_C$  [°C]:

$$C_0 = -(C_3 T_C^3 + C_2 T_C^2 + C_1 T_C^1). \quad (6)$$

It is likely that the temperature effect on the sensor electronics varies from sensor to sensor, thus the coefficients derived herein (the average of the three sensors; error bars are shown in Fig. 2) may not yield the most accurate temperature correction for all sensors of the same model.



**Figure 2:** Empirically-measured temperature responses of the soil and fast-response O<sub>2</sub> sensors, with third order polynomials fit to the data points, compared to the theoretical temperature response calculated from the ideal gas law (Eq. (1)). The difference between the theoretical and measured responses is due to a temperature effect on the sensor electronics. The polynomial coefficients used to correct for the temperature response with Eq. (5) are listed. An offset coefficient ( $C_0$ ) is not listed because it is dependent on the temperature at calibration. It is calculated with Eq. (6). The sensors were calibrated at 20 °C. As with barometric pressure, the absolute O<sub>2</sub> concentration, and thus the O<sub>2</sub> sensor output, varies with temperature. As temperature changes the relative O<sub>2</sub> concentration remains constant at 20.95 %, but an apparent O<sub>2</sub> change is measured if the temperature correction is not applied to relative measurements.

### Effect of Humidity on Gas Concentration

As the humidity in the atmosphere increases, water vapor molecules displace and dilute other gas molecules, including O<sub>2</sub> molecules. This causes the output of a sensor to decrease. The effect of water vapor displacement of O<sub>2</sub> is larger at warmer temperatures because the capacity of air to hold water is greater and there is more water vapor in the air. The water vapor effect on relative O<sub>2</sub> concentration as a function of relative humidity ( $RH$ ) and at a constant temperature (Fig. 3A) is a linear decrease with increasing  $RH$ . Conversely, the effect as a function of temperature at constant  $RH$  is a curvilinear decrease with increasing temperature (Fig. 3B), essentially the inverse of the slope of the vapor pressure curves from the psychrometric chart. Even though water vapor molecules dilute and displace O<sub>2</sub> molecules, and thus cause an actual and not an apparent decrease in relative O<sub>2</sub> concentration, humidity effects are accounted for to yield relative O<sub>2</sub> concentrations for a dry atmosphere. The equation to correct for humidity effects is:

$$O_2 = O_{2M} \left[ 1 + \left( \frac{e_{AM} - e_{AC}}{BP_C} \right) \right] \quad (7)$$

where  $BP_C$  is as given above,  $e_{AM}$  is the vapor pressure [kPa] of the air at the time of measurement, and  $e_{AC}$  is the vapor pressure [kPa] of the air at calibration. The vapor pressures in Eq. (7) are calculated from:

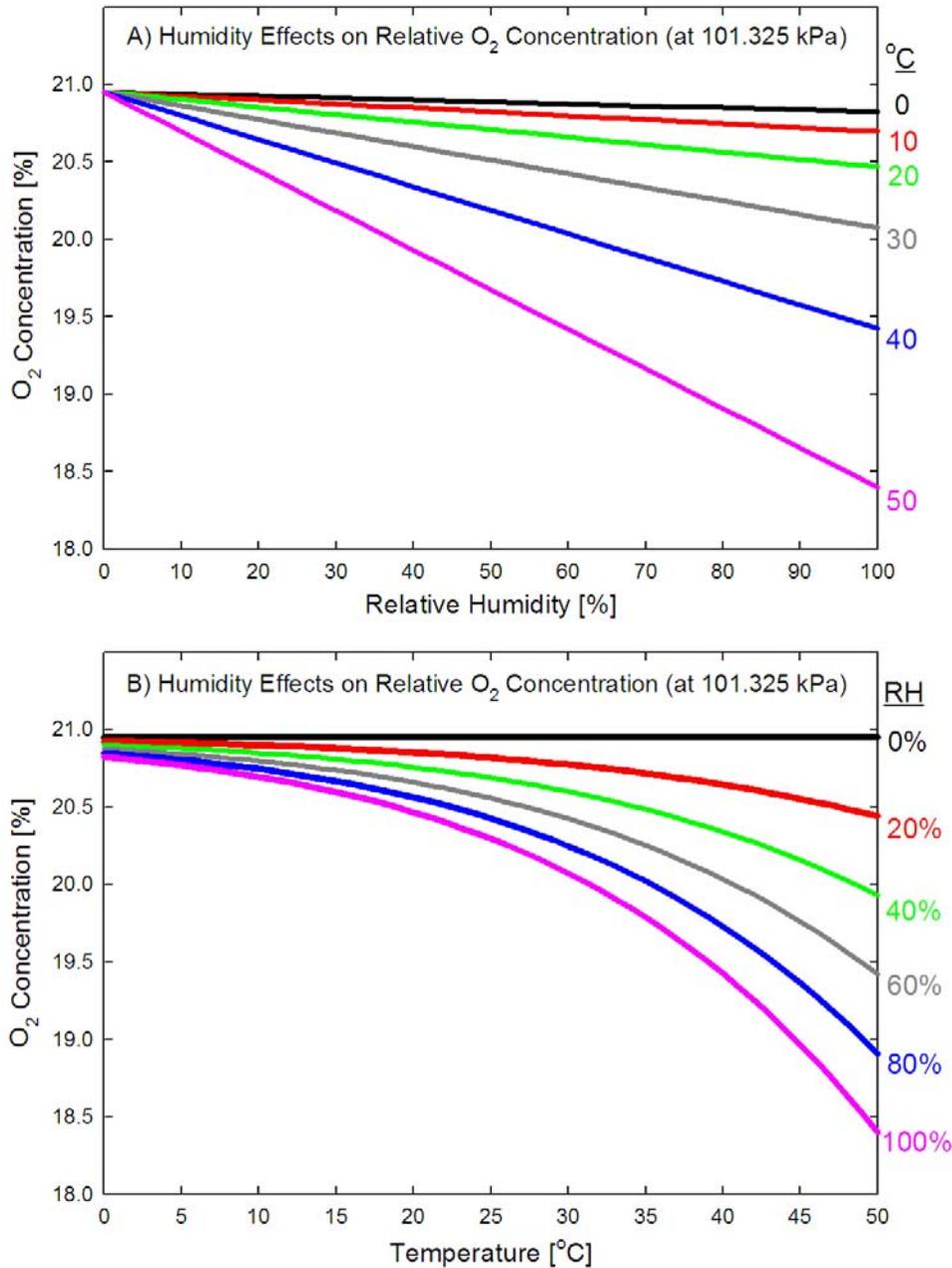
$$e_A = e_S \left( \frac{RH}{100} \right) \quad (8)$$

where  $RH$  is in % and  $e_S$  is the saturation vapor pressure [kPa] of the air calculated from air temperature ( $T_A$ ) [ $^{\circ}C$ ]:

$$e_S = 0.61121 \exp \left( \frac{17.502 T_A}{240.97 + T_A} \right). \quad (9)$$

In soil environments  $RH$  is generally always 100 %, unless the soil is extremely dry. Thus, the water vapor effect can be accounted for as a function of temperature by correcting  $O_2$  measurements based on the shape of the curve for 100 %  $RH$ .

As with temperature, humidity also causes a slight effect on the sensor electronics. It is recommended that for measurements in soil or saturated air ( $RH = 100$  %), the sensor be calibrated in conditions where the  $RH = 100$  %. A simple way to accomplish this is to mount the sensor in a sealed chamber over water (Fig. 4).



**Figure 3:** A) Relative humidity (*RH*) effects on relative O<sub>2</sub> concentration shown as a function of *RH* at temperatures increments of 10 °C and B) as a function of temperature at *RH* increments of 20 %. The air in soil is generally always saturated with water vapor unless the soil is very dry.

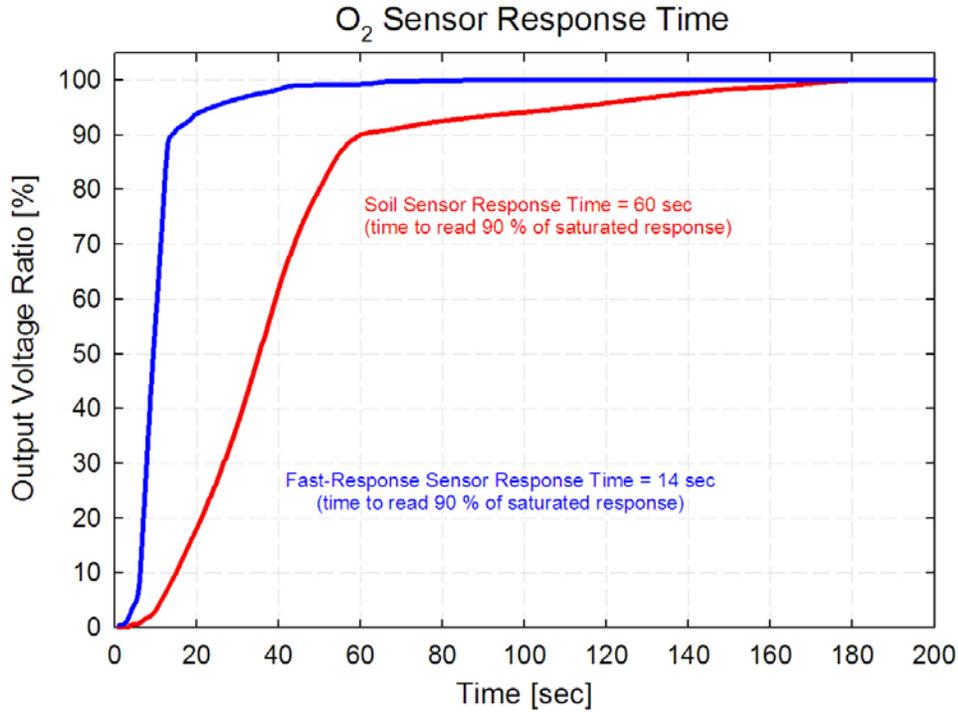


**Figure 4:** Apogee O<sub>2</sub> sensor mounted in a sealed chamber over water. For measurements in environments where the  $RH = 100\%$ , sensors should be calibrated in conditions where the  $RH = 100\%$  in order to account for any humidity effects on sensor electronics.

### **Sensor Description and Calibration**

Apogee O<sub>2</sub> sensors are galvanic cell sensors with a lead anode, gold cathode, acid electrolyte, and Teflon membrane (membrane where O<sub>2</sub> diffusion occurs). The current flow between the two electrodes is linearly proportional to the absolute amount of O<sub>2</sub> in the environment being measured. An internal bridge resistor is used to produce a voltage output rather than a direct current output. Galvanic cell sensors consume a small amount of gas in order to produce the current flow between the electrodes and subsequent voltage output. The O<sub>2</sub> consumption from Apogee O<sub>2</sub> sensors was measured to be 2.1 μmol per day at 20.95 % O<sub>2</sub> and at an average temperature of 20 °C in a small sealed chamber.

All sensors are equipped with an internal thermistor or type-K thermocouple for reference temperature measurement. The sensors also come equipped with a small resistance heater located behind the Teflon membrane inside the sensor. The heaters are designed to warm the sensor to a temperature slightly above ambient in order to keep condensation from occurring on the membrane under conditions where the  $RH$  is 100 %. The response time of the soil sensor is 60 seconds versus 14 seconds for the fast-response sensor (Fig. 5). The response time is defined as the time required for the sensor to read 90 % of the saturated response.



**Figure 5:** Response times for both Apogee O<sub>2</sub> sensor models (soil sensor and fast-response sensor). The response time is defined as the time required for the sensor to read 90 % of the saturated response (60 seconds for the soil sensor and 14 seconds for the fast-response sensor).

The output signal for the soil sensor is approximately 58.0 mV under typical atmospheric conditions (20.95 % O<sub>2</sub> and 101.325 kPa) and the signal decrease is reported as 1.0 mV per year (< 2.0 % per year) (Fig. 6). The output signal for the fast-response sensor is approximately 12.8 mV under typical atmospheric conditions and the signal decrease is reported as 0.8 mV per year (6 % per year up to 5 years) (Fig. 6).

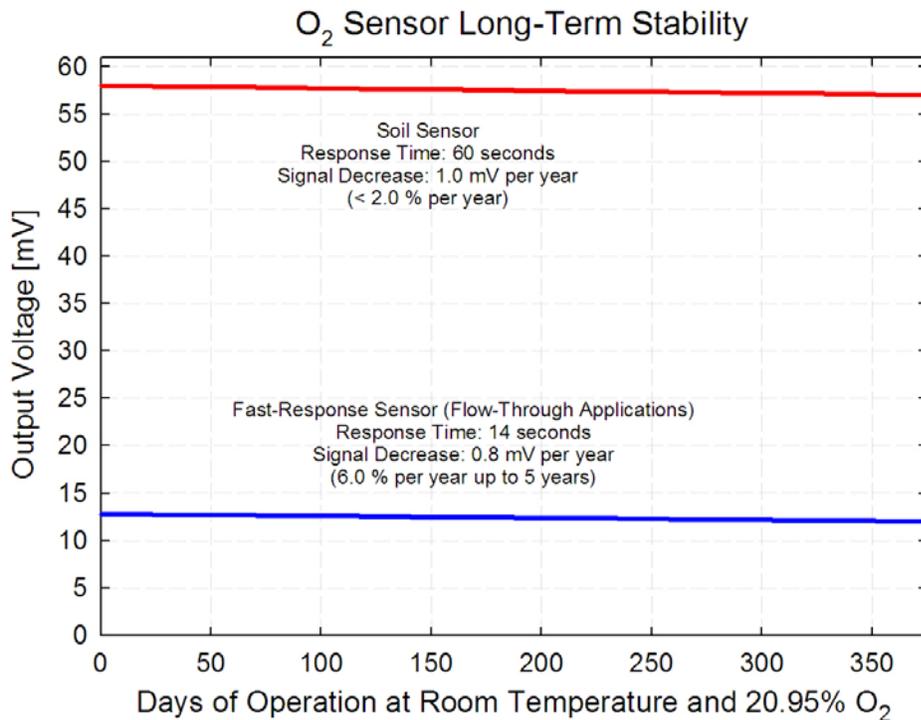
The output of Apogee O<sub>2</sub> sensors is a linear function of absolute O<sub>2</sub> concentration. A simple linear calibration is generally used to derive a calibration factor used to convert the output from the sensor to relative O<sub>2</sub> concentration. The calibration factor ( $CF$ ) [% O<sub>2</sub> / mV] is derived by simply dividing ambient O<sub>2</sub> concentration (20.95 %) by the measured voltage output from the sensor under ambient conditions (in air or over water in a sealed chamber) minus the measured voltage output under conditions of 0 % O<sub>2</sub>:

$$CF = \frac{20.95\%}{mV_C - mV_0} \quad (10)$$

where  $mV_C$  is the output [mV] of the sensor during calibration,  $mV_0$  is the voltage output [mV] under 0 %  $O_2$ , and  $CF$  is a linear multiplier that converts subsequent voltage measurements from the sensor to %  $O_2$  using the equation:

$$O_2 = CF \cdot mV_M - Offset \quad (11)$$

where  $mV_M$  is the measured output [mV] and Offset is derived by multiplying  $CF$  by  $mV_0$ . If  $mV_0$  is not measured it can be assumed to be 2.5 mV for the soil sensor and 0.25 mV for the fast-response sensor. It is recommended that  $mV_0$  be measured (in pure  $N_2$  gas) for applications where low values of  $O_2$  (< 15 %) will be measured.



**Figure 6:** Long-term stability (output voltage decrease over time) of both Apogee O<sub>2</sub> sensor models (soil and fast response sensors). The response time and signal decrease are also listed for the two models.