

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 [mol m^{-3}]:

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

where P is pressure [Pa], V is volume [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 [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 (O_2) in the atmosphere, assuming there is no water vapor in the atmosphere, is 0.2095 kPa O_2 per kPa air or 20.95 %. The atmospheric concentration of 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 O_2 concentration does not remain constant. An O_2 tank is required to climb Mount Everest, even though the relative O_2 concentration is still 20.95 % (Fig. 1A). The absolute O_2 concentration determines the rate of most biological and chemical processes, but the relative 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.

Absolute Amount of Gas	Relative Amount of Gas
moles of O_2 per unit volume (e.g. moles per Liter)	% O_2 in air (e.g. 20.95 % in ambient air)
mass of O_2 per unit volume (e.g. grams per Liter; O_2 has a mass of 32 g per mole)	mole fraction (e.g. moles of O_2 per mole of air; 0.2095 mol O_2 per mole of ambient air; this can also be expressed as 0.2095 kPa O_2 per kPa air)
partial pressure (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 O_2 increase of 0.207 % ($0.00987 * 20.95 \% =$

0.207 %) and an apparent relative O₂ 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 O₂ increase. In this example, 0.247 % O₂ for every 1 kPa increase in barometric pressure (0.0118 * 20.95 % = 0.243 %) and an apparent relative O₂ concentration of 21.193 %.

A barometric pressure correction should be applied to all O₂ sensors that are calibrated to read relative O₂ concentration. The equation to correct O₂ 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 O₂ concentration [%] (the apparent O₂ 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 O₂ 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 O₂ measurement as a change in relative O₂ concentration because sensors respond to absolute O₂ concentration, but are generally calibrated to read relative O₂ concentration.

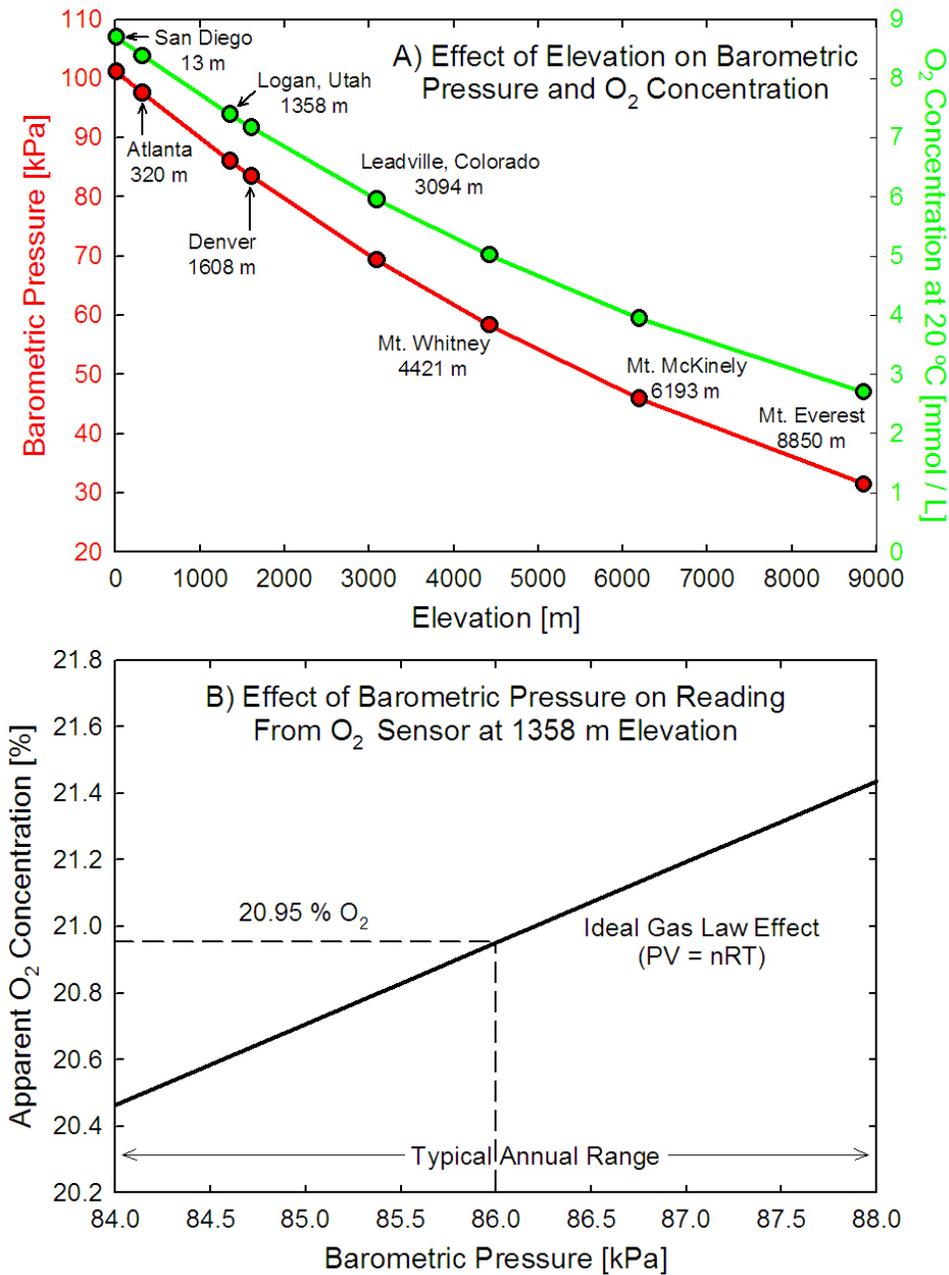


Figure 1: A) Barometric pressure and absolute O₂ concentration [mmol / L] at 20 °C as a function of elevation. Equation (3) was used to calculate barometric pressure. B) The effect of barometric pressure on apparent relative O₂ concentration (O₂ concentration measured with an O₂ sensor). O₂ sensors respond to absolute O₂ concentration but are generally calibrated to yield relative O₂ concentration. As the barometric pressure fluctuates, the absolute O₂ concentration, and thus the O₂ sensor output, fluctuates with it, producing an apparent change in the relative O₂ 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 O₂ 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 % O₂ (0.341 % * 0.2095 = 0.0714 %) and a relative O₂ concentration of 20.8786 %. As with barometric pressure, to obtain accurate O₂ measurements a correction should be applied to compensate for temperature effects. The equation to correct O₂ 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 O₂ 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 O₂ concentration because sensors respond to absolute O₂ concentration but are calibrated to read relative O₂ 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 O₂ sensors (soil and fast response sensors) was determined from measurements in dry air across a wide temperature range by plotting pressure-corrected apparent O₂ concentration (i.e., measured O₂ 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 O₂ 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.

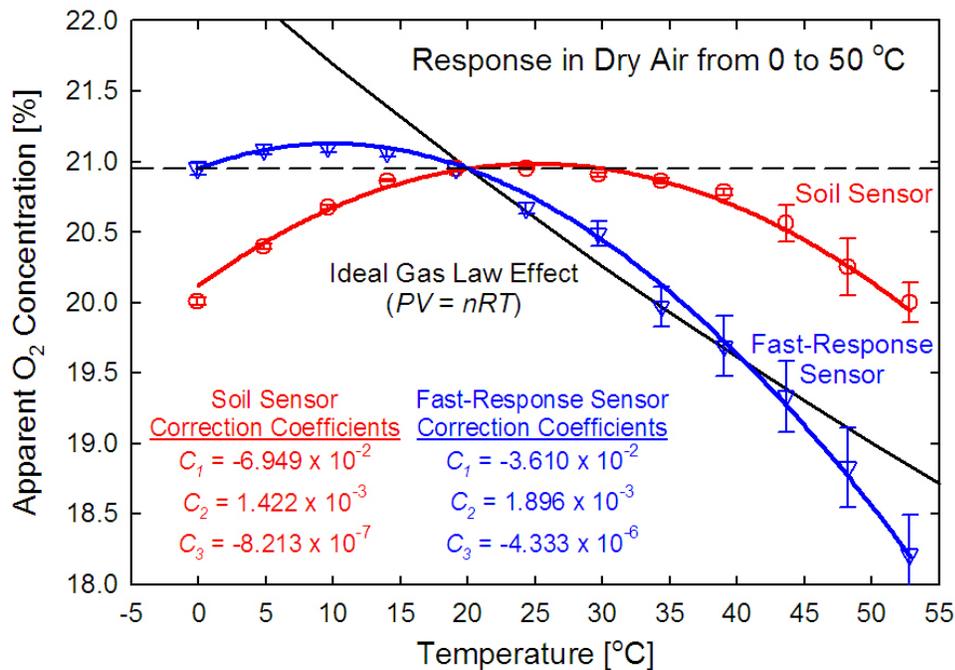


Figure 2: Empirically-measured temperature responses of the soil and fast-response O₂ sensors, with third order polynomials fit to the data points, compared to the theoretical temperature response calculated from the ideal gas law (Eq. (1)). The difference between the theoretical and measured responses 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 O₂ concentration, and thus the O₂ sensor output, varies with temperature. As temperature changes the relative O₂ concentration remains constant at 20.95 %, but an apparent O₂ 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 O₂ molecules. This causes the output of a sensor to decrease. The effect of water vapor displacement of O₂ 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 O₂ 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 O₂ molecules, and thus cause an actual and not an apparent decrease in relative O₂ concentration, humidity effects are accounted for to yield relative O₂ 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).

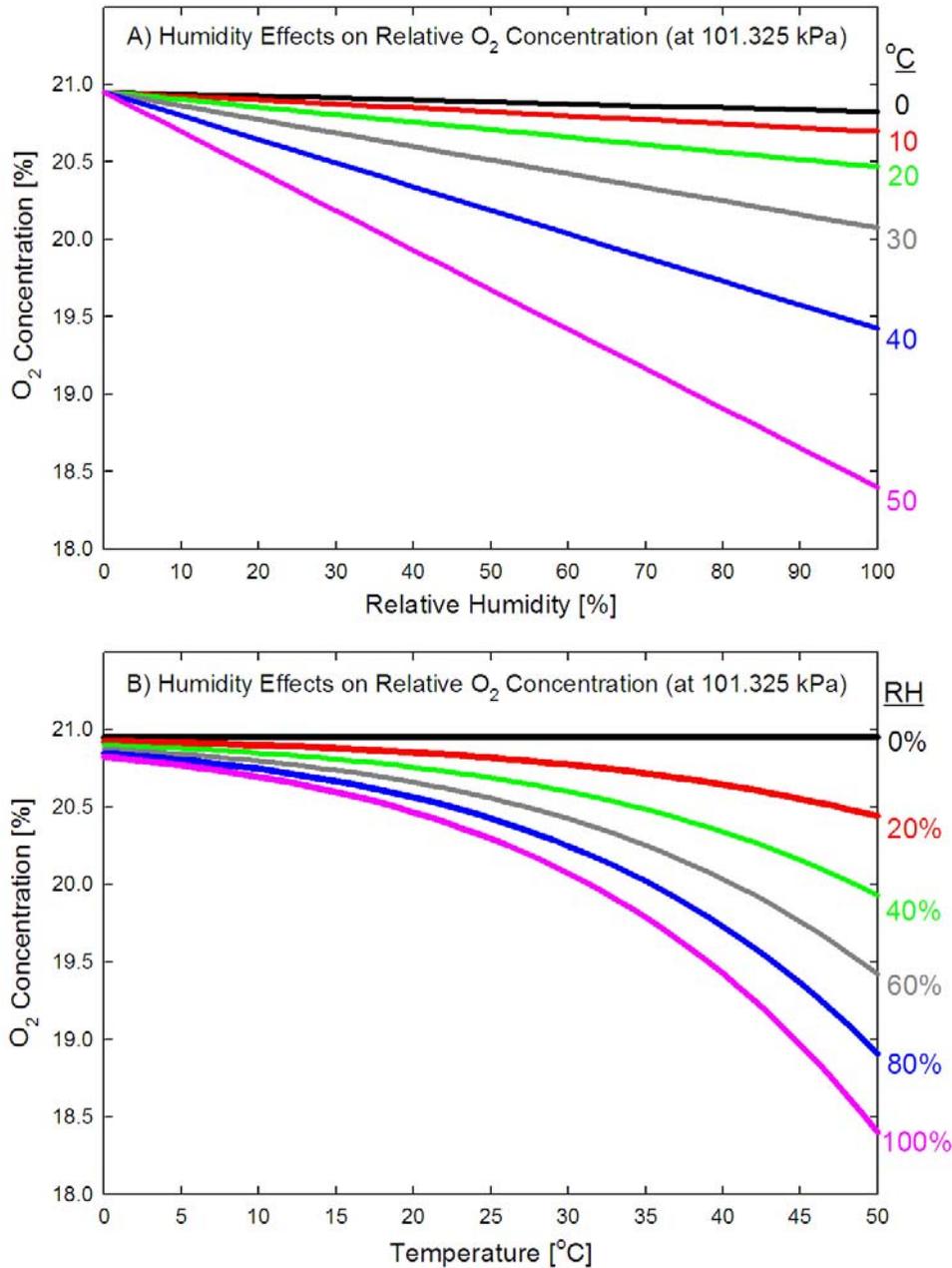


Figure 3: A) Relative humidity (*RH*) effects on relative O₂ concentration shown as a function of *RH* at temperatures increments of 10 °C and B) as a function of temperature at *RH* increments of 20 %. The air in soil is generally always saturated with water vapor unless the soil is very dry.



Figure 4: Apogee O₂ 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 O₂ sensors are galvanic cell sensors with a lead anode, gold cathode, acid electrolyte, and Teflon membrane (membrane where O₂ diffusion occurs). The current flow between the two electrodes is linearly proportional to the absolute amount of O₂ 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 O₂ consumption from Apogee O₂ sensors was measured to be 2.1 μmol per day at 20.95 % O₂ 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.

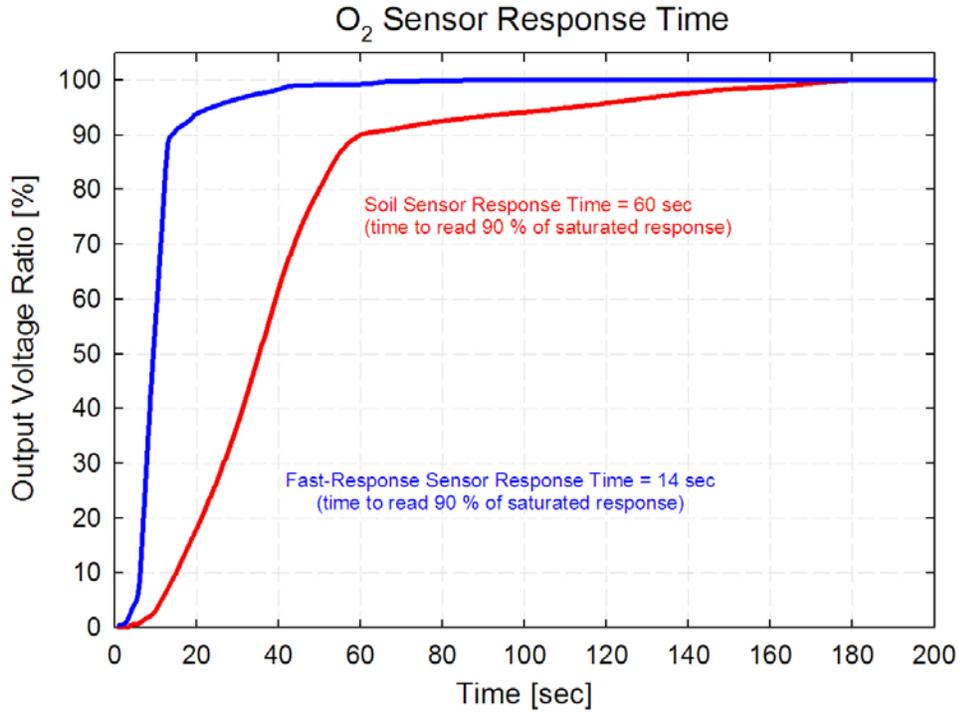


Figure 5: Response times for both Apogee O₂ sensor models (soil sensor and fast-response sensor). The response time is defined as the time required for the sensor to read 90 % of the saturated response (60 seconds for the soil sensor and 14 seconds for the fast-response sensor).

The output signal for the soil sensor is approximately 58.0 mV under typical atmospheric conditions (20.95 % O₂ 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 O₂ sensors is a linear function of absolute O₂ concentration. A simple linear calibration is generally used to derive a calibration factor used to convert the output from the sensor to relative O₂ concentration. The calibration factor (CF) [% O₂ / mV] is derived by simply dividing ambient O₂ 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 % O₂:

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

where mV_C is the output [mV] of the sensor during calibration, mV_0 is the voltage output [mV] under 0 % O₂, and CF is a linear multiplier that converts subsequent voltage measurements from the sensor to % O₂ 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 N₂ gas) for applications where low values of O₂ (< 15 %) will be measured.

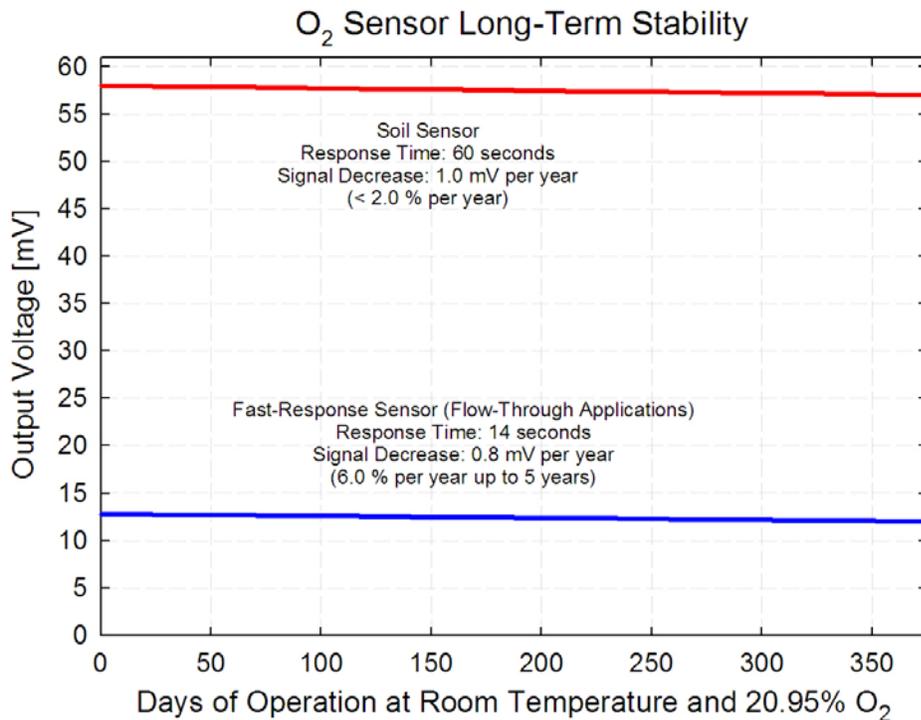


Figure 6: Long-term stability (output voltage decrease over time) of both Apogee O₂ sensor models (soil and fast response sensors). The response time and signal decrease are also listed for the two models.