

Recommendations on the conversion between oxygen quantities for Bio-Argo floats and other autonomous sensor platforms

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Fixed a typo in S_{corr} and added clarification on S_{preset} use in salinity correction, October 2017

Fixed a type in the exponent of B_2 in S_{corr} , April 2018

Recommended implementation

A. Conversion from mL L^{-1} (MLPL_DOXY) to $\mu\text{mol L}^{-1}$ (MOLAR_DOXY)

This conversion is required to convert Sea-Bird oxygen sensor data given in mL O_2 (gas at S.T.P) per L of seawater (i.e., MLPL_DOXY in $\text{mL}_{\text{STP}} \text{L}^{-1}$) into $\mu\text{mol O}_2$ per L of seawater (i.e., MOLAR_DOXY in $\mu\text{mol L}^{-1}$). The conversion is valid both for salinity-corrected and salinity-uncorrected O_2 data.

$$c_{\text{O}_2} (\mu\text{mol L}^{-1}) = 44.6596 \cdot c_{\text{O}_2} (\text{mL}_{\text{STP}} \text{L}^{-1})$$

The molar volume of oxygen used here is $22.3916 \text{ L}_{\text{STP}} \text{mol}^{-1}$ (Garcia and Gordon 1992). Its reciprocal gives the conversion factor of $44.6596 \mu\text{mol mL}_{\text{STP}}^{-1}$.

B. Conversion from mg L^{-1} to $\mu\text{mol L}^{-1}$ (MOLAR_DOXY)

For some applications, oxygen concentration is given as mass O_2 per L of seawater, e.g., mg L^{-1} . The molar weight of O_2 determines the conversion factor to $\mu\text{mol O}_2$ per L of seawater (i.e., MOLAR_DOXY in $\mu\text{mol L}^{-1}$). The conversion is valid both for salinity-corrected and salinity-uncorrected O_2 data.

$$c_{\text{O}_2} (\mu\text{mol L}^{-1}) = 31.2512 \cdot c_{\text{O}_2} (\text{mg L}^{-1})$$

The molar weight of O_2 used here is $31.9988 \text{ g mol}^{-1}$ (CIAAW 2015). Its reciprocal gives the conversion factor of $31.2512 \mu\text{mol mg}^{-1}$.

C. Conversion from salinity-uncorrected MOLAR_DOXY optode data to salinity-corrected, molar oxygen concentration $c_{\text{O}_2}(T,S)$

Oxygen optodes are insensitive to the salinity S of the ambient seawater, while the O_2 amount they measure follows the salinity dependence of the seawater O_2 solubility $c_{\text{O}_2}^*(T,S)$. Their initial O_2 concentration output $c_{\text{O}_2}(T, S_{\text{preset}})$ (e.g., MOLAR_DOXY; default $S_{\text{preset}} = 0$) thus needs to be salinity-compensated to yield the correct O_2 concentration $c_{\text{O}_2}(T,S)$. The correction relates the initial concentration output $c_{\text{O}_2}(T, S_{\text{preset}})$ to the seawater concentration (at T and S) that has the same partial pressure. The correction term S_{corr} is the salinity-dependent part of $c_{\text{O}_2}^*(T,S)$ according to Garcia and Gordon (1992), using the Benson and Krause refit coefficients. The Benson and Krause (1984) data is considered to be more accurate than the other datasets and recommended for general use (Garcia and Gordon 1992; Wong and Li

2009). The Garcia and Gordon (1992) parameterization gives the O_2 concentration in equilibrium with an atmosphere of standard composition saturated with vapor pressure at a total pressure (including that of the water vapor) of 1 atm. The water vapor pressure changes with the salt content (colligative effect), i.e., the atmospheric composition (O_2 content) at a total pressure of 1 atm (including water vapor) is different at S_{preset} and S . The water vapor terms account for that difference.

Note: The water vapor term is often not taken into account by optode manufacturer / optode on-board calculations. In that case, S_{preset} only in the water vapor term needs to be replaced with 0.

$$\text{salinity-corrected } c_{O_2}(T,S) = S_{\text{Corr}} \cdot \frac{1013.25 - p_{H_2O}(T,S_{\text{preset}})}{1013.25 - p_{H_2O}(T,S)} \cdot \text{salinity-uncorrected } c_{O_2}(T,S_{\text{preset}})$$

$$S_{\text{Corr}} = \exp((S - S_{\text{preset}}) \cdot (B_0 + B_1 \cdot T_s + B_2 \cdot T_s^2 + B_3 \cdot T_s^3) + C_0 \cdot (S^2 - S_{\text{preset}}^2))$$

$$T_s = \ln((298.15 - T) / (273.15 + T))$$

$$B_0 = -6.24523e-3$$

$$B_1 = -7.37614e-3$$

$$B_2 = -1.03410e-2$$

$$B_3 = -8.17083e-3$$

$$C_0 = -4.88682e-7$$

(Garcia and Gordon 1992, Benson and Krause refit)

$$p_{H_2O} = 1013.25 \cdot \exp(D_0 + D_1 \cdot \left(\frac{100}{T_{\text{abs}}}\right) + D_2 \cdot \ln\left(\frac{T_{\text{abs}}}{100}\right) + D_3 \cdot S)$$

$$D_0 = 24.4543$$

$$D_1 = -67.4509$$

$$D_2 = -4.8489$$

$$D_3 = -5.44e-4$$

(Weiss and Price 1980)

$$T_{\text{abs}} = T + 273.15$$

where

T = temperature (°C)

S = salinity (dimensionless, Practical Salinity Scale 1978)

S_{preset} = salinity of the uncorrected oxygen concentration (dimensionless, PSS-78; default: 0)

p_{H_2O} = water vapor pressure (mbar)

T_{abs} = absolute temperature (K)

D. Conversion from salinity-uncorrected MOLAR_DOXY optode data to partial pressure pO_2

This conversion will be required for surface/air measurements by oxygen optodes reporting salinity-uncorrected MOLAR_DOXY. It makes use of equation (4) of the background section (see below). The oxygen solubility $c_{O_2}^*(T,S)$ can be separated into a temperature-dependent part T_{Corr} and a salinity-dependent part S_{Corr} ,

$$c_{O_2}^*(T,S) = T_{\text{Corr}} \cdot S_{\text{Corr}}$$

Combining equations (4) and (5) with the conversion C (with $S_{\text{preset}} = 0$) between salinity-corrected and uncorrected oxygen concentration, the S_{Corr} term drops out and the conversion below remains. It includes the effect of hydrostatic pressure on pO_2 , which is negligible near the surface.

Note: The water vapor term is often not taken into account by optode manufacturer / optode on-board calculations. In that case, S_{preset} in the water vapor term needs to be replaced with 0.

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$$pO_2 = c_{O_2}(T, S_{\text{preset}}) \cdot \frac{x_{O_2} \cdot (1013.25 - p_{H_2O}(T, S_{\text{preset}}))}{T_{\text{Corr}}} \cdot \exp\left(\frac{V_m \cdot P}{R \cdot T_{\text{abs}}}\right)$$

$$x_{O_2} = 0.20946 \quad (\text{Glueckauf 1951})$$

$$T_{\text{Corr}} = 44.6596 \cdot \exp(A_0 + A_1 \cdot T_s + A_2 \cdot T_s^2 + A_3 \cdot T_s^3 + A_4 \cdot T_s^4 + A_5 \cdot T_s^5)$$

$$A_0 = 2.00907$$

$$A_1 = 3.22014$$

$$A_2 = 4.05010$$

$$A_3 = 4.94457$$

$$A_4 = -2.56847e-1$$

$$A_5 = 3.88767 \quad (\text{Garcia and Gordon 1992, Benson and Krause refit})$$

$$V_m = 0.317 \quad (\text{Enns et al. 1965})$$

$$R = 8.314 \quad (\text{CODATA 2014})$$

where

pO_2 = oxygen partial pressure (mbar)
 $c_{O_2}(T, S_{\text{preset}})$ = salinity-uncorrected oxygen concentration at $S=S_{\text{preset}}$ ($\mu\text{mol L}^{-1}$)
 T = Temperature ($^{\circ}\text{C}$)
 S_{preset} = salinity of the uncorrected oxygen concentration (dimensionless, PSS-78; default: 0)
 x_{O_2} = mixing ratio of oxygen in dry air (dimensionless)
 V_m = molar volume of oxygen ($\text{m}^3 \text{mol}^{-1} \text{Pa dbar}^{-1}$)
 P = hydrostatic pressure (dbar)
 R = universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)

E. Conversion from molar oxygen concentration $c_{O_2}(T, S)$ to oxygen partial pressure pO_2

This conversion between salinity-corrected oxygen concentration $c_{O_2}(T, S)$ and partial pressure pO_2 follows equations 4 and 5 of the background section, i.e.,

$$pO_2 = c_{O_2}(T, S) \cdot \frac{x_{O_2} \cdot (1013.25 - p_{H_2O}(T, S))}{T_{\text{Corr}} \cdot S_{\text{Corr}}} \cdot \exp\left(\frac{V_m \cdot P}{R \cdot T_{\text{abs}}}\right)$$

where

pO_2 = oxygen partial pressure (mbar)
 $c_{O_2}(T, S)$ = salinity-corrected oxygen concentration ($\mu\text{mol L}^{-1}$)

All other terms required (x_{O_2} , p_{H_2O} , T_{Corr} , S_{Corr} , V_m , R , T_{abs}) are given above with references.

F. Conversion from molar oxygen concentration $c_{O_2}(T, S)$ to oxygen concentration DOXY on the molinity scale

This conversion is just added for completeness in an Argo framework, to give the final fully corrected O_2 concentration in units of molinity, i.e., $\mu\text{mol kg}^{-1}$ seawater (DOXY).

$$c_{O_2} (\mu\text{mol kg}^{-1}) = c_{O_2} (\mu\text{mol L}^{-1}) / \rho$$

where

ρ = potential density of seawater (kg L^{-1}) referenced to a hydrostatic pressure of 0 dbar and using practical salinity. We recommend using the equation of state based on Fofonoff and Millard (1983) and Millero et al. (1980).

Background

(based on Bittig et al. 2015: Pressure Response of Aanderaa and Sea-Bird Oxygen Optodes. *J. Atmos. Oceanic Techn.* **32(12)** 2305–2317, doi:10.1175/JTECH-D-15-0108.1)

Oxygen saturation can be expressed both in terms of oxygen concentration as the ratio of c_{O_2} to O_2 solubility $c_{\text{O}_2}^*$, and in terms of partial pressure as the ratio of water $p\text{O}_2$ to the atmospheric equilibrium partial pressure $p\text{O}_{2,\text{air}}$,

$$\text{sat O}_2 = \frac{c_{\text{O}_2}}{c_{\text{O}_2}^*} = \frac{p\text{O}_2}{p\text{O}_{2,\text{air}}} . \quad (1)$$

Equation 1 can thus be used to easily convert between concentrations and partial pressures. At the sea surface, $p\text{O}_{2,\text{air}}$ follows

$$p\text{O}_{2,\text{air}} = x\text{O}_2 \cdot (p_{\text{air}} - p\text{H}_2\text{O}) , \quad (2)$$

where $p\text{H}_2\text{O}$ is the saturation water vapor pressure after Weiss and Price (1980) and $x\text{O}_2 = 0.20946$ the mixing ratio of O_2 in dry air (Glueckauf 1951). $p\text{O}_{2,\text{air}}$ and thus O_2 saturation are therefore dependent on the ambient atmospheric pressure p_{air} as well as on saturation water vapor pressure which is a function of seawater temperature and salinity. The temperature (T) and salinity (S) dependent seawater O_2 solubility $c_{\text{O}_2}^*(\text{T},\text{S})$ is given for a pressure of one atmosphere (Garcia and Gordon 1992) and needs to be scaled to ambient pressure for surface applications according to

$$c_{\text{O}_2}^*(\text{T},\text{S},p_{\text{air}}) = c_{\text{O}_2}^*(\text{T},\text{S}) \cdot \frac{p_{\text{air}} - p\text{H}_2\text{O}(\text{T},\text{S})}{1013.25 \text{ mbar} - p\text{H}_2\text{O}(\text{T},\text{S})} \quad (3)$$

in order to yield the correct saturation (equ. 1). In the above equation, only components other than water vapor are scaled since $p\text{H}_2\text{O}$ depends on temperature and salinity only but not on atmospheric pressure p_{air} .

Inserting (2) and (3) into (1) yields

$$c_{\text{O}_2} = \frac{c_{\text{O}_2}^*(\text{T},\text{S})}{x\text{O}_2 \cdot (1013.25 \text{ mbar} - p\text{H}_2\text{O}(\text{T},\text{S}))} \cdot p\text{O}_2 \quad (4)$$

i.e., the conversion of partial pressure $p\text{O}_2$ to O_2 concentration c_{O_2} is independent of p_{air} (since the change in O_2 saturation cancels out).

Below the surface, hydrostatic pressure P affects both the oxygen solubility and partial pressure. Enns et al. (1965) describe an exponential increase in $p\text{O}_2$ of about 14 % per 1000 dbar and Taylor (1978) provides a theoretical relationship,

$$p\text{O}_2(\text{P}) = p\text{O}_2 \cdot \exp\left(\frac{V_{\text{m}}(\text{O}_2) \cdot \text{P}}{R \cdot (\text{T} + 273.15 \text{ K})}\right) \quad (5)$$

where $V_{\text{m}}(\text{O}_2) = 31.7 \text{ mL mol}^{-1}$ is the molar volume of O_2 in seawater (Enns et al. 1965) and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ the universal gas constant. The $p\text{O}_2$ increase with hydrostatic pressure reflects a higher outgassing tendency with depth, i.e., a reduced solubility $c_{\text{O}_2}^*(\text{T},\text{S},\text{P})$. Consequently, equ. 5 and 4 need to be combined for the conversion between $p\text{O}_2(\text{P})$ and c_{O_2} for sub-surface applications. For the solubility follows

$$c_{O_2}^*(T,S,P,p_{air}) = c_{O_2}^*(T,S) \cdot \frac{p_{air} - p_{H_2O}(T,S)}{1013.25 \text{ mbar} - p_{H_2O}(T,S)} / \exp\left(\frac{V_m(O_2) \cdot P}{R \cdot (T + 273.15 \text{ K})}\right). \quad (6)$$

As a consequence, the conversion from oxygen concentration or oxygen partial pressure to oxygen saturation depends on temperature T, salinity S, hydrostatic pressure P, and the ambient air pressure p_{air} .

Especially the last quantity poses a challenge for subsurface applications since p_{air} is no conservative tracer that easily tracks with the water mass from its formation region nor is it easily measurable. Commonly, one atmosphere (1013.25 mbar) as default is used as a workaround. However, a value of "100 % saturation at 1 atm" is incompatible with the interpretation of "being in equilibrium with the atmosphere" over most portions of the ocean. As an example, p_{air} over the Southern Ocean is typically (significantly) below one atmosphere. There, "100 % saturation at 1 atm" would consistently give supersaturated waters relative to equilibrium, i.e., "100 % saturation at local atmospheric pressure". When working with oxygen saturations, it is thus essential to state the reference state, 1 atm or ambient p_{air} , together with the saturation value to indicate whether the scaling of equation 3 has been performed or not.

Nomenclature

Oxygen concentration, c_{O_2} : amount of O_2 in a given volume (molarity, $\mu\text{mol L}^{-1}$) or mass of seawater (molinity, $\mu\text{mol kg}^{-1}$)

Oxygen partial pressure, p_{O_2} : gas pressure of O_2 in a gas mixture (mbar)

Oxygen solubility, $c_{O_2}^*$: The saturation equilibrium concentration of O_2 with air at ambient conditions of temperature T, salinity S, air pressure p_{air} , and hydrostatic pressure P. Laboratory experimental values are tabulated at zero dbars hydrostatic pressure, P, and an air pressure, p_{air} , of one atmosphere (1013.25 mbar). Units are the same as for concentration.

Oxygen saturation, $\text{sat } O_2$: ratio of the O_2 amount present in a given sample and its equilibrium O_2 concentration (i.e., ratio of c_{O_2} and $c_{O_2}^*$, or ratio of p_{O_2} to the equilibrium air p_{O_2} ; see eq. 1). This value is also frequently presented as the percent difference from saturation equilibrium, i.e., $\Delta O_2 (\%) = (c_{O_2} - c_{O_2}^*) / c_{O_2}^* \cdot 100 \%$.

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