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July 13, 2011

Office of Water Quality Technical Memorandum 2011.03

Subject: Change to Solubility Equations for Oxygen in Water

This memorandum announces and describes changes to the equations that traditionally have been used by the U.S. Geological Survey (USGS) to predict the solubility of dissolved oxygen (DO) in water. The DO solubility tables in Chapter 6 of the *National Field Manual for the Collection of Water-Quality Data* (NFM), as well as all of the software that compute oxygen solubility that are being used or in development by the USGS, will be revised accordingly within fiscal year 2011 or the first quarter of fiscal year 2012 (table 1).

The Office of Water Quality (OWQ) has received inquiries regarding slight discrepancies between values predicted for DO solubility by USGS tables and computer programs compared with values computed by following the methods listed in *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, 2005) (*Standard Methods*). In 2010, the OWQ asked Stewart Rounds of the USGS Oregon Water Science Center to investigate the source of these discrepancies and provide the OWQ with an analysis and recommendation.

Stewart Rounds' analysis resulted in a well-documented recommendation to replace the Weiss (1970)¹ equations with the equations developed by Benson and Krause (1980, 1984). His analysis and recommendation received rigorous review by David Parkhurst and Judson Harvey, geochemists with the USGS National Research Program. Consequently, the recommendation to adopt the Benson-Krause equations has been accepted by OWQ. Adopting the Benson-Krause equations will eliminate the discrepancies noted between USGS methods and those cited in *Standard Methods* and bring us into conformity with the methods that currently are in wide use by the science community, while having no significant effect on the use of USGS historical data.

The attachment to this memorandum describes in detail the rationale and scientific underpinning for replacing the Weiss (1970) equations with those by Benson and Krause (1980, 1984).

¹ References cited and additional references used in the preparation of this Technical Memorandum are listed at the end of the Attachment.

Table 1. Documents and software slated for DO solubility equation revision

| Report or software | Revision by or before | Revised by |
|-----------------------------------|------------------------------|-----------------------|
| NFM, Chapter.6, Section 6.2 | 9/30/2011 | Stewart Rounds |
| DOTABLES | 7/31/2011 | Stewart Rounds |
| PCFF | 11/30/2011 | Frank Crenshaw |
| NAWQA metabolism | 12/31/2011 | Jerad Bales |
| Data Grapher | Done | Stewart Rounds |
| CHIMP | 12/31/2011 | Burl Goree |
| National Park Service spreadsheet | 9/30/2011 | National Park Service |

Contact Information

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Chief, Office of Water Quality

This memorandum updates Quality of Water Branch Technical Memorandum 81.11.

Distribution: All WRD Employees

Attachment: Analysis to Support the Replacement of Weiss (1970) Equations by Benson and Krause (1980, 1984) Equations for USGS Computation of Solubility of Dissolved Oxygen in Water

ATTACHMENT

Analysis to Support the Replacement of Weiss (1970) Equations by Benson and Krause (1980, 1984) Equations for USGS Computation of Solubility of Dissolved Oxygen in Water

Background and Rationale for Action

Since 1981, the USGS has computed the solubility of oxygen in water based largely on equations developed by Weiss (1970). The Weiss equations were documented in Quality of Water Branch Technical Memorandums 81.11 (<http://water.usgs.gov/admin/memo/QW/qw81.11.html>) and 81.15 (<http://water.usgs.gov/admin/memo/QW/qw81.15.html>). Although the Weiss equations produce relatively accurate results for oxygen solubility, other formulations for computing oxygen solubility have become available since 1970 that are more accurate and have become more generally accepted. The equations published by Benson and Krause (1980, 1984) are based on data as well as derivations from thermodynamic principles and fit the available data somewhat better than the Weiss equations. The Benson and Krause equations have gained wide acceptance in the science community and are cited by *Standard Methods* (2005).

Differences in the predictions between Weiss (1970) and Benson and Krause (1980, 1984) are small and are expected always to be less than the increments (0.1 to 0.2 mg/L) that typically are used when reporting measurements of dissolved oxygen. Comparisons of predicted oxygen solubility between the methods of Weiss and Benson and Krause indicate differences of as much as 0.03 mg/L for freshwater at sea level, and an average of 0.01 mg/L over a range of environmental temperatures. Current and future improvements in measurement technology, however, dictate that these small differences may become more important. These discrepancies and other errors would be eliminated by adopting the Benson-Krause oxygen solubility equations. In addition, use by the USGS of the Benson-Krause equations would be consistent with the equations cited in the latest edition of *Standard Methods* (2005), which are widely accepted and used by the science community.

Based on the following rationale, it is the decision of the Office of Water Quality that the USGS replace the oxygen-solubility equations developed by Weiss (1970) with those of Benson and Krause (1980, 1984) and amend the various tables and computer programs used by the USGS to reflect this change:

- (1) Results in an increase in accuracy of DO solubility determinations for waters typically monitored by the USGS,
- (2) Promotes practices consistent with the best scientific methods that currently are accepted within the science community, and
- (3) Small differences in measurement accuracy can be expected to become more important with advances in measurement technology.

Analysis and Summary of Formulations for Oxygen Solubility

Several sets of equations are available for the computation of oxygen solubility in freshwater and seawater. Three are summarized and compared in this memorandum:

Weiss, 1970,
Benson and Krause, 1980 and 1984, and
Garcia and Gordon, 1992

All three sets of equations apply to a temperature range of 0–40 °C, a salinity range of 0–40‰, and a pressure range of 0.5–1.1 atmospheres (380–836 mm Hg).

Other formulations also have been published over the years, including a relatively new one by Geng and Duan (2010) that is derived from thermodynamic principles and covers a much wider range of temperature and pressure. For natural waters, however, it does not seem necessary at this time to consider a new and somewhat untested approach that spans a range of conditions that are well beyond those typically encountered during USGS investigations.

The equations in the sections below are summarized in the following form:

$$[DO] = DO_o * F_s * F_p, \quad (1)$$

where the dissolved oxygen (DO) concentration in mg/L is represented as a baseline concentration in freshwater (DO_o) multiplied by a salinity correction factor (F_s) and a pressure correction factor (F_p). All three terms are a function of water temperature. In addition, the salinity correction factor is a function of salinity and the pressure correction factor is a function of barometric pressure. For freshwater (salinity=0‰) and standard pressure (1 atm), the salinity and pressure factors are equal to 1.0.

The Benson and Krause (1980, 1984) oxygen-solubility formulations (now adopted by USGS) are documented in equations 1 and 7 through 11 of this Attachment to the Technical Memorandum. Equation 4 is retained as a means of estimating salinity from specific conductance.

The Weiss Equations

In his 1970 publication, Weiss proposed a set of equations to compute oxygen solubility in water as a function of water temperature and salinity. The Weiss equations were based on the best measurements of dissolved-oxygen solubility available at the time (for example, Carpenter, 1966). Those equations estimate oxygen solubility as a function of water temperature and salinity; other equations were applied by USGS to compute the dependence of oxygen solubility on barometric pressure. The Weiss equations compute a result in units of mL/L, and a factor was used to convert that result to mg/L. Unfortunately, the factor used by USGS since 1981 was based on an incorrect assumption that the Weiss results were for an *ideal* gas at standard temperature and pressure (STP: 1 atm, 0 °C). In fact, Weiss intended his results to be expressed as the volume occupied by oxygen as a *real* (non-ideal) gas at STP (see Benson and Krause, 1980). Therefore, the 1.4276 factor used by USGS in Technical Memorandum 81.11 to convert mL/L to mg/L is incorrect; that factor should have been 1.42905 mg/mL. This mistake by itself accounts for an error of approximately 0.007–0.015 mg/L for freshwater at 1 atm and a temperature range of 0–40 °C.

The Weiss baseline DO concentration at zero salinity and one atmosphere is:

$$DO_o = 1.42905 \exp \left[-173.4292 + 249.6339 \left(\frac{100}{T} \right) + 143.3483 \left(\ln \left(\frac{T}{100} \right) \right) - 21.8492 \left(\frac{T}{100} \right) \right], \quad (2)$$

where T is the water temperature in Kelvin ($T = t(^{\circ}\text{C}) + 273.15$) and the resulting DO concentration is in mg/L. **Note that the first factor in equation 2 (1.42905) was incorrectly specified as 1.4276 in Technical Memorandum 81.11, and all applications of the Weiss equations by the USGS as of March 10, 2011 contained that error, including DOTABLES, PCFF, the oxygen-saturation script by the North Carolina Water Science Center, and the Data Grapher.** The National Park Service duplicated the erroneous factor in their spreadsheet calculator for percent DO saturation.

The Weiss salinity factor is:

$$F_s = \exp \left\{ S * \left[-0.033096 + 0.014259 \left(\frac{T}{100} \right) - 0.0017000 \left(\frac{T}{100} \right)^2 \right] \right\}, \quad (3)$$

where S is the salinity in parts per thousand (‰) and T is temperature in Kelvin. This salinity factor was derived with the assumption that the dissolved ions in the water are identical to those present in seawater. Equations 2 and 3 are the Weiss (1970) equations.

To convert a measurement of specific electrical conductance (SC) to salinity, Technical Memorandum 81.11 suggests the following equation:

$$S = 5.572 \times 10^{-4} (SC) + 2.02 \times 10^{-9} (SC)^2, \quad (4)$$

where SC is specific conductance in microsiemens per centimeter ($\mu\text{S}/\text{cm}$) at 25 °C. Equation 4 is an approximation, but it captures the general characteristics of a far more complex set of equations relating salinity to conductance (and temperature) as published in *Standard Methods* (American Public Health Association, 2005). Differences between the predictions of equation 4 and equations from *Standard Methods* typically result in less than a 0.1 percent change in the salinity factor of equation 3 over a wide range of temperature (0-40 °C) and specific conductance (0-67,000 $\mu\text{S}/\text{cm}$).

Although Technical Memorandum 81.11 indicates that the errors associated with equation 4 are not significant for most applications, the actual error depends on the composition of the water. Substantial concentrations of multivalent ions will cause the relation between specific conductance and salinity to deviate from that in equation 4. If the solubility of oxygen must be computed for brines or brackish waters that have ionic compositions far different from that of seawater, then the general equations documented in this Technical Memorandum may not apply, and other equations for oxygen solubility should be used, such as those developed by Millero and others (2002a, 2002b).

The pressure factor specified by USGS in Technical Memorandum 81.11 is:

$$F_p = \frac{P - u}{760 - u}, \quad (5)$$

where P is the barometric pressure in mm Hg and u is the vapor pressure of water in mm Hg. An empirical relation for the vapor pressure of water in mm Hg was presented in Technical Memorandum 81.11 as:

$$u = 10^{\left(8.10765 - \frac{1750.286}{235+t}\right)}, \quad (6)$$

where t is the water temperature in degrees Celsius.

The Benson and Krause Equations

Benson and Krause derived a series of equations from thermodynamic principles that compute the solubility of oxygen in water. Because the resulting theoretical equations are relatively complicated, they decided to fit their theoretical data to a simpler set of equations. Their first paper specifies oxygen solubility as a function of temperature in freshwater only (Benson and Krause, 1980), whereas their second paper includes adjustments based on barometric pressure and salinity (Benson and Krause, 1984). To compute the oxygen solubility in mg/L, their baseline DO concentration at zero salinity and one atmosphere is:

$$DO_o = \exp\left[-139.34411 + \frac{1.575701 \times 10^5}{T} - \frac{6.642308 \times 10^7}{T^2} + \frac{1.243800 \times 10^{10}}{T^3} - \frac{8.621949 \times 10^{11}}{T^4}\right], \quad (7)$$

where T is the water temperature in Kelvin ($T = t(^{\circ}\text{C}) + 273.15$). The Benson and Krause salinity factor is:

$$F_s = \exp\left[-S * \left(0.017674 - \frac{10.754}{T} + \frac{2140.7}{T^2}\right)\right], \quad (8)$$

where S is salinity in parts per thousand (‰) and T is temperature in Kelvin. As with the Weiss equations, salinity can be estimated from specific conductance using equation 4, as long as the ionic composition of the water is not substantially different from that of seawater.

The pressure factor derived by Benson and Krause is similar to the factor specified in Technical Memorandum 81.11, but includes an additional correction factor for non-ideal gases:

$$F_p = \frac{(P-u)(1-\theta_o P)}{(1-u)(1-\theta_o)}, \quad (9)$$

where P is the barometric pressure in atmospheres, u is the vapor pressure of water in atmospheres, and θ_o is related to the second virial coefficient of oxygen:

$$\theta_o = 0.000975 - 1.426 \times 10^{-5} t + 6.436 \times 10^{-8} t^2, \quad (10)$$

where t is temperature in degrees Celsius. Benson and Krause (1980) provide an equation for the vapor pressure of water in atmospheres:

$$u = \exp\left(11.8571 - \frac{3840.70}{T} - \frac{216961}{T^2}\right), \quad (11)$$

where T is water temperature in Kelvin.

The Garcia and Gordon Equations

Garcia and Gordon (1992) examined the data used by Benson and Krause (1984) as well as others, and re-fitted those data with a higher order polynomial. Their equations result in a better fit to the data, but the added refinement may not be necessary or worthwhile for USGS work (see the comparisons in the next section). The baseline DO concentration at zero salinity and one atmosphere specified by Garcia and Gordon is:

$$DO_o = 1.42905 \exp\left(2.00907 + 3.22014T_s + 4.05010T_s^2 + 4.94457T_s^3 - 0.256847T_s^4 + 3.88767T_s^5\right), \quad (12)$$

where T_s is a scaled temperature defined as:

$$T_s = \ln\left(\frac{298.15 - t}{273.15 + t}\right) \quad (13)$$

and t is water temperature in degrees Celsius. The salinity factor derived by Garcia and Gordon is:

$$F_s = \exp\left[\left(-0.00624523 - 0.00737614T_s - 0.0103410T_s^2 - 0.00817083T_s^3\right)S - 4.88682 \times 10^{-7} S^2\right], \quad (14)$$

where S is salinity in parts per thousand (‰) and T_s is the scaled temperature defined above. Salinity may be estimated from specific conductance by using the approximation provided in Technical Memorandum 81.11 and reproduced as equation 4 above. Pressure corrections could be applied by using the Benson and Krause factors given in equations 9–11.

Comparison of Predictions

Temperature Dependence. In figure 1 below, the baseline DO_o predictions of Weiss (equation 2), Benson and Krause (equation 7), and Garcia and Gordon (equation 12) from the previous sections are compared to an independent dataset of thermodynamic predictions of oxygen solubility derived by Benson and Krause (1980, 1984). Recall that equations 7–11 shown above for Benson and Krause are a simplified polynomial fit to the results of their more complex thermodynamic derivations. The comparisons in figure 1 are made for standard pressure (1 atm) and freshwater (zero salinity).

The Garcia and Gordon equations clearly provide the best fit to the thermodynamic derivations, with a maximum error of about 0.0002 mg/L, but the errors inherent to the thermodynamic derivation might be larger. The maximum error in the polynomial fit by Benson and Krause is on the order of 0.001 mg/L, an error that is relatively small and acceptable for most USGS investigations. The Weiss equations produce a larger error, with the maximum error in the range of 0.019–0.034 mg/L, depending on whether the real or ideal gas conversion factor is used. Relative errors for the Benson and Krause equations are less than 0.01 percent, but as high as 0.25 percent for the Weiss equations with the real gas conversion factor.

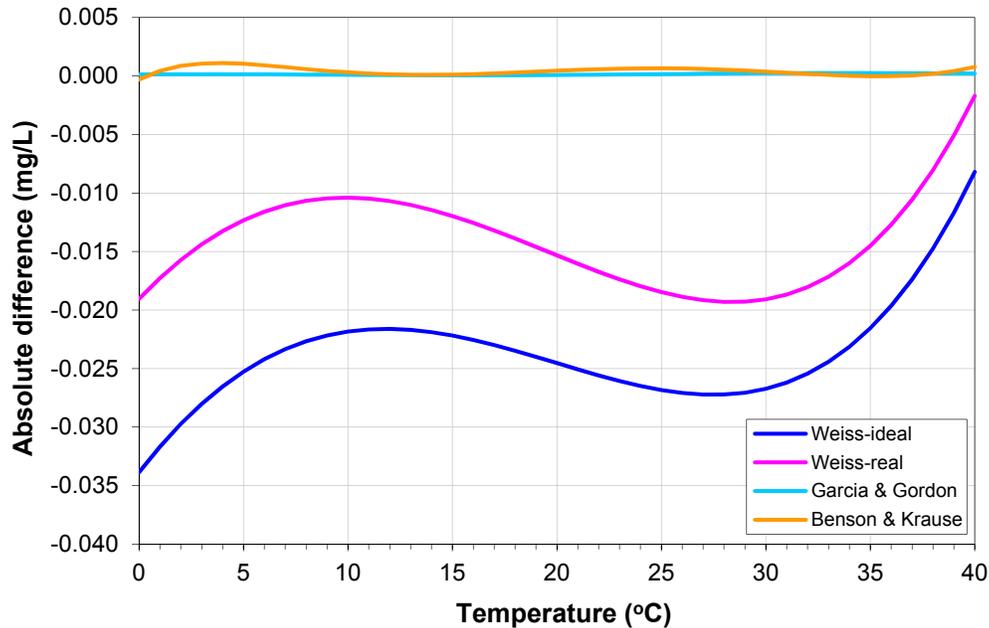


Figure 1. Graph showing the absolute difference in predicted oxygen solubility at 1.0 atmosphere pressure and zero salinity for several sets of predictive equations, where that absolute difference is relative to the thermodynamic derivations of Benson and Krause (1980, 1984). Two curves are plotted for the Weiss equations, showing the importance of the real or ideal gas conversion factor (USGS has been using the ideal gas conversion factor).

These comparisons indicate that the Weiss equations can be improved. Given that DO measurement equipment often is calibrated to the nearest 0.01 mg/L, the equations used by USGS to predict oxygen solubility need to be accurate to within 0.01 mg/L. If the thermodynamic derivations of Benson and Krause are accurate, then the Weiss equations may not be sufficiently accurate for the calibration of DO sensors, despite providing predictions that are within several hundredths of a milligram per liter.

Salinity Factor. The salinity correction factors from Weiss (equation 3) and Garcia and Gordon (equation 14) are compared to the salinity correction factor from Benson and Krause (equation 8) in figures 2 and 3, respectively. The comparisons span a salinity range of 0-40‰ and a temperature range of 0-40 °C, and the differences are expressed as a relative percent deviation from the Benson and Krause predictions.

The Weiss salinity correction factor is most similar to the Benson and Krause factor in the 17-31 °C range, but deviates more strongly at cooler and warmer temperatures and at higher salinities (figure 2). The Garcia and Gordon salinity correction factor is much more similar to the Benson and Krause salinity factor, with relative differences less than 0.03 percent (figure 3). In contrast, the Weiss salinity correction factor differs from the Benson and Krause factor by as much as 0.66 percent over the same range of temperatures and salinities. At 0 °C, 1 atm, and 40‰, that difference can be as large as 0.06 mg/L.

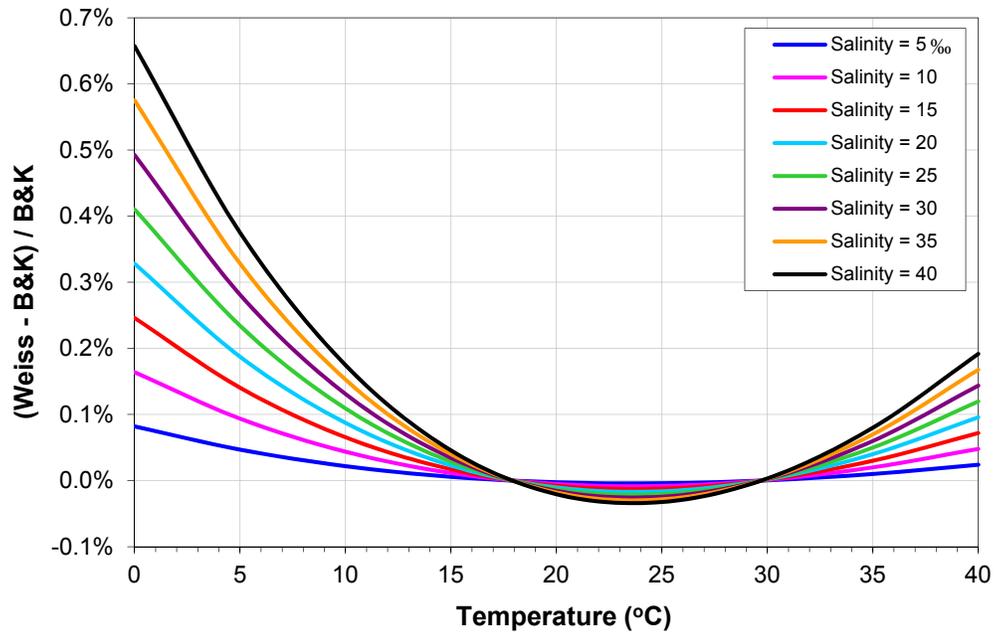


Figure 2. Graph showing the relative percent difference between the Weiss salinity correction factor and the Benson and Krause salinity correction factor over a range of temperatures (0–40 °C) and salinities (5–40‰). The maximum difference for these conditions is 0.66 percent, but only about 0.03 percent in the 17–31 °C temperature range.

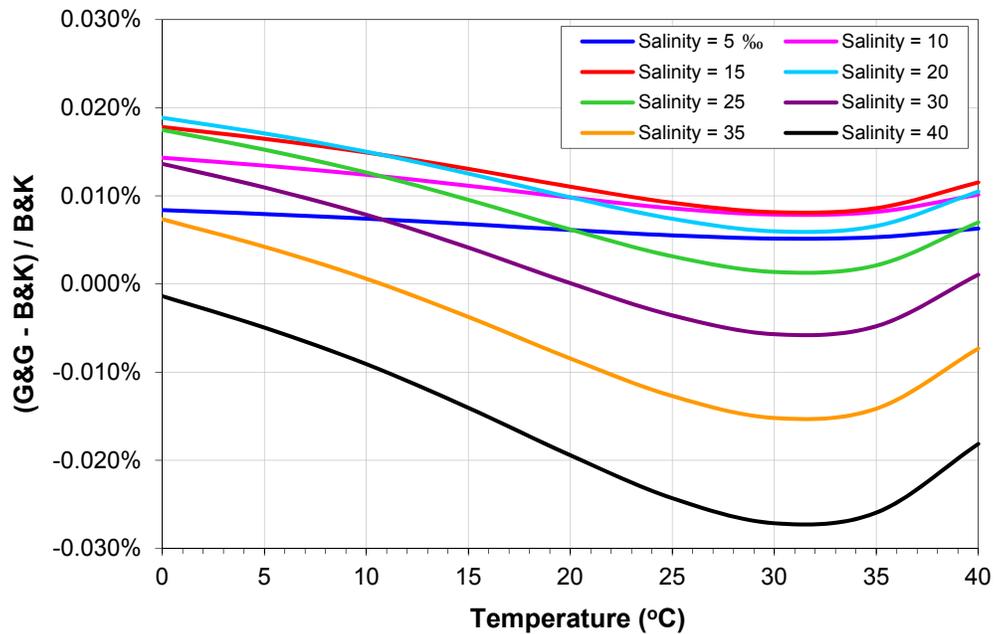


Figure 3. Graph showing the relative percent difference between the Garcia and Gordon salinity correction factor and the Benson and Krause salinity correction factor over a range of temperatures (0–40 °C) and salinities (5–40‰). The maximum difference for these conditions is less than 0.03 percent.

Pressure Factor. The pressure correction factor used by USGS (equations 5–6) is compared to the pressure correction factor derived by Benson and Krause (equations 9–11) in figure 4 for a range of temperatures (0–40 °C) and pressures (600–800 mm Hg). The results show that the USGS pressure corrections are quite similar to those derived by Benson and Krause, with greater differences as the pressure deviates further from 1 atm (760 mm Hg), but a maximum difference of only 0.02 percent for the range of conditions shown. The differences in figure 4 are caused primarily by the non-ideal gas correction factor in the Benson and Krause formulation—the factors containing θ_o in equation 9. The differences in the pressure factor resulting from different equations used to estimate the vapor pressure of water (equations 6 and 11) are negligible—less than 0.0005 percent for the conditions tested.

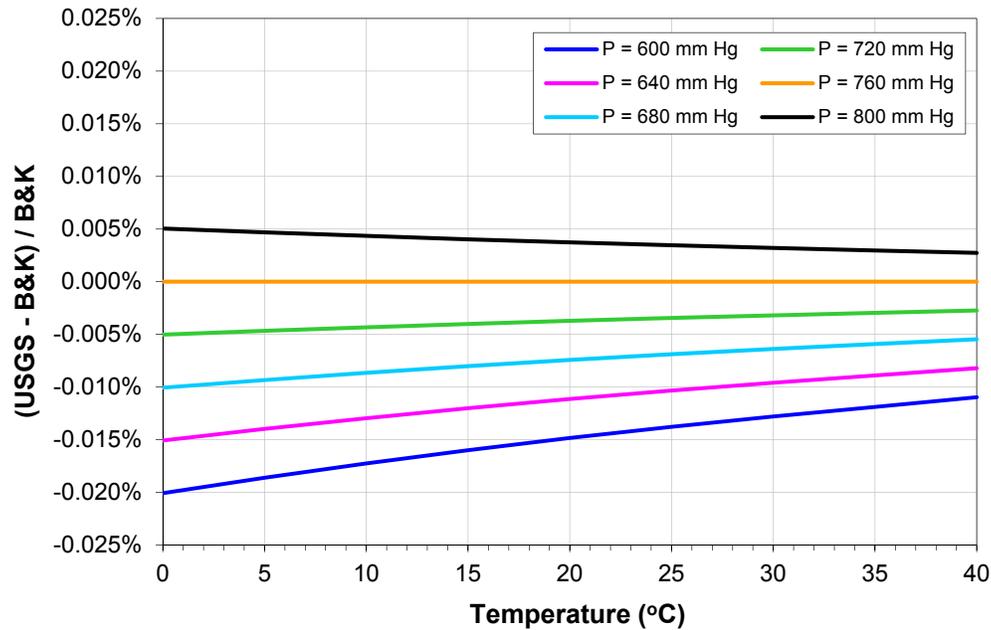


Figure 4. Graph showing the relative percent difference between the USGS pressure correction factor and the Benson and Krause pressure correction factor over a range of temperatures (0–40 °C) and pressures (600–800 mm Hg). The maximum difference for these conditions is less than 0.02 percent.

Updated Oxygen Solubility Predictions

The oxygen solubility concentrations predicted by Benson and Krause (equations 1 and 7 through 11) are plotted in figures 5 and 6 as a function of water temperature, salinity, and barometric pressure.

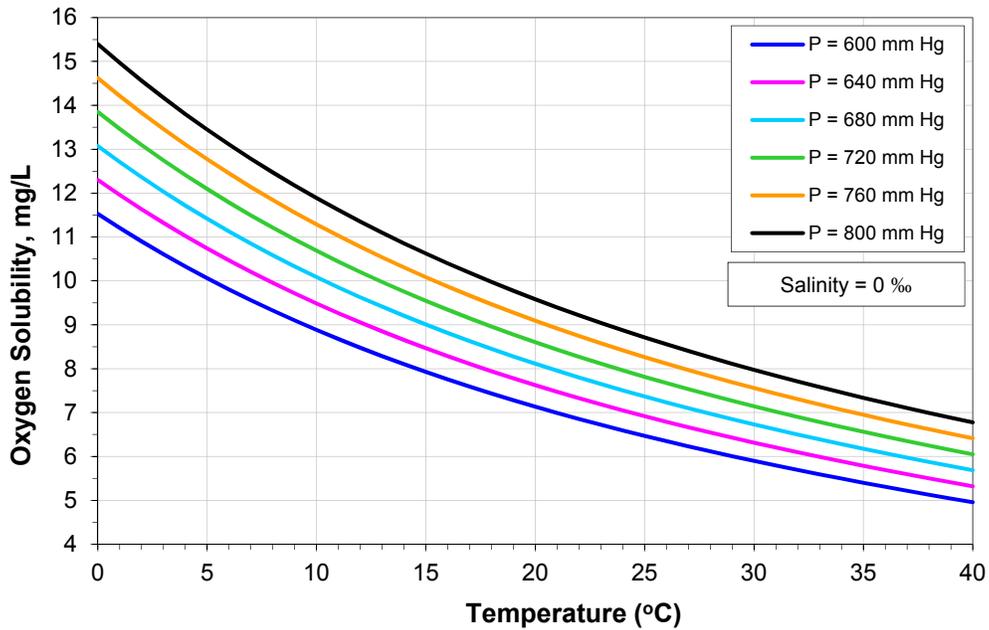


Figure 5. Graph showing the predicted solubility of oxygen in freshwater (salinity = 0‰) as a function of water temperature and barometric pressure using the Benson and Krause (1980, 1984) formulas embodied in equations 1 and 7-11 of this Technical Memorandum.

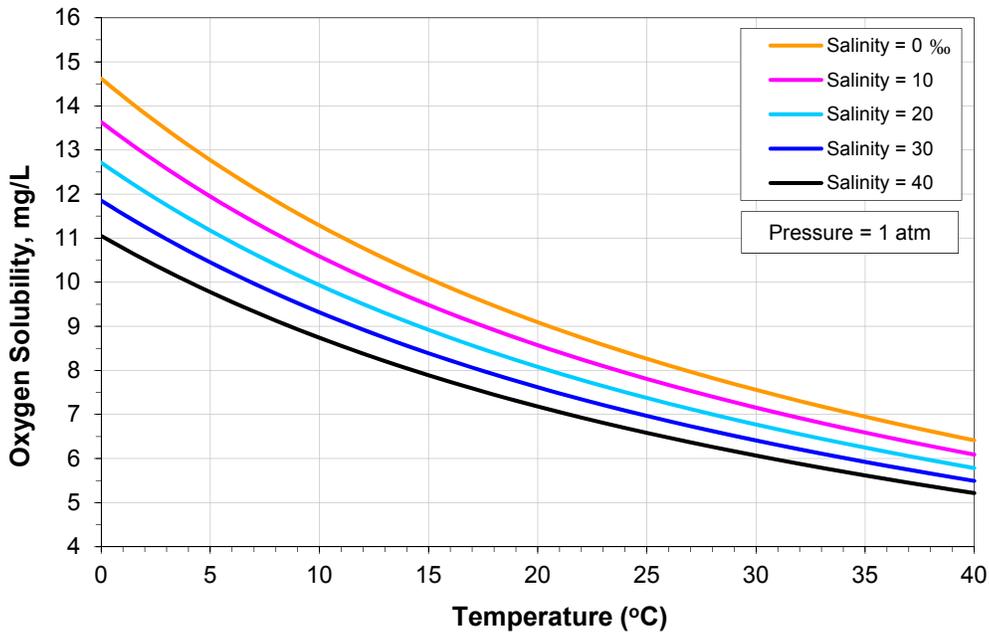


Figure 6. Graph showing the predicted solubility of oxygen in water at 1 atmosphere (760 mm Hg) as a function of water temperature and salinity using the Benson and Krause (1980, 1984) formulas embodied in equations 1 and 7-11 of this Technical Memorandum.

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² An asterisk (*) indicates a reference that is not cited in this Technical Memorandum.

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