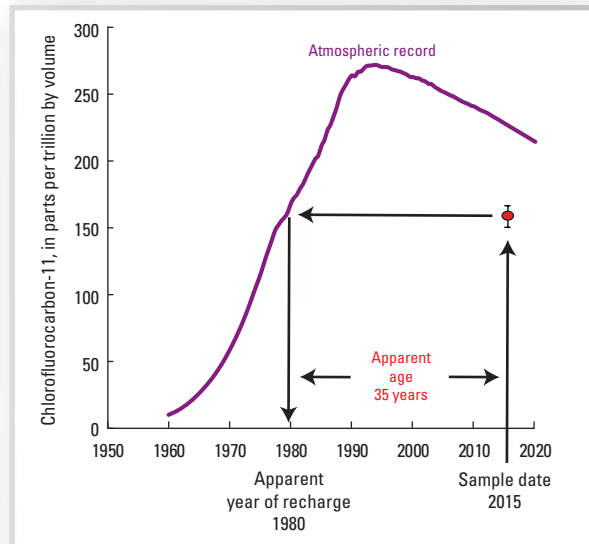
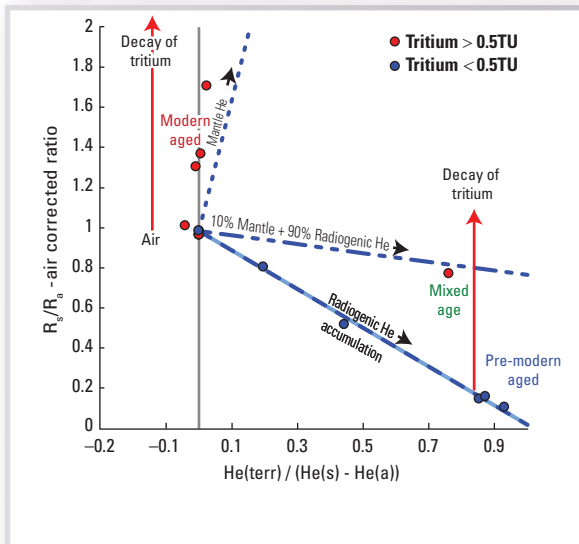
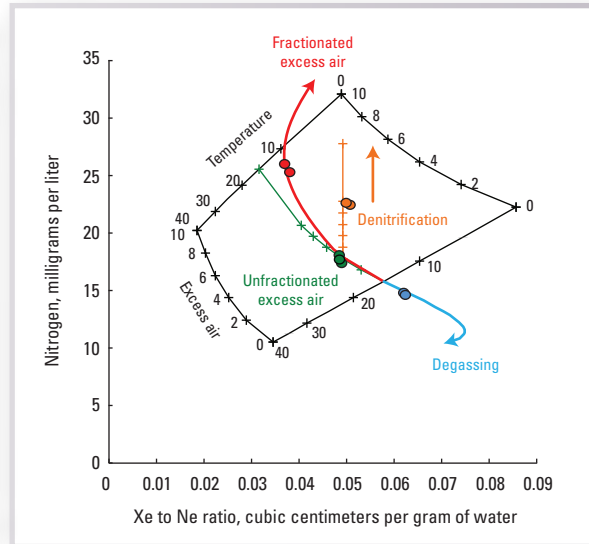
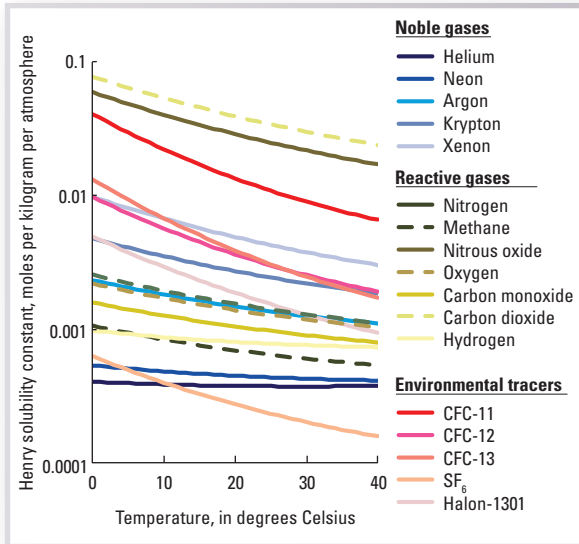


National Water Quality Assessment Project

DGMETA (Version 1): Dissolved Gas Modeling and Environmental Tracer Analysis Computer Program



Techniques and Methods 4-F5

Cover Photos:

Solubility constant of gases
(in freshwater) included in
the program.

Plot of gases from samples and
paths of dissolved gas models.

Analysis of helium isotope
systematics.

Use of the environmental
tracers for determining age
of the water.

DGMETA (Version 1): Dissolved Gas Modeling and Environmental Tracer Analysis Computer Program

By Bryant C. Jurgens, J.K. Böhlke, Karl Haase, Eurybiades Busenberg, Andrew G. Hunt, and Jeffrey A. Hansen

National Water Quality Assessment Project

Techniques and Methods 4-F5

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
DAVID BERNHARDT, Secretary

U.S. Geological Survey
James F. Reilly II, Director

U.S. Geological Survey, Reston, Virginia: 2020

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Conversion Factors

International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
meter (m)	3.281	foot (ft)
Volume		
cubic meter (m ³)	6.290	barrel (petroleum, 1 barrel = 42 gal)
liter (L)	33.81402	ounce, fluid (fl. oz)
cubic meter (m ³)	264.2	gallon (gal)
cubic meter (m ³)	0.0002642	million gallons (Mgal)
cubic centimeter (cm ³)	0.06102	cubic inch (in ³)
liter (L)	61.02	cubic inch (in ³)
cubic meter (m ³)	35.31	cubic foot (ft ³)
cubic meter (m ³)	1.308	cubic yard (yd ³)
cubic meter (m ³)	0.0008107	acre-foot (acre-ft)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
kilopascal (kPa)	0.009869	atmosphere, standard (atm)
Energy		
joule (J)	0.0000002	kilowatthour (kWh)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Datum

Elevation, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance (SC) is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$).

Activities for radioactive constituents in water are given in picocuries per liter (pCi/L).

Salinity (S) is given in parts per thousand (per mil).

^3He and ^4He . The element helium (He) has atoms with different masses: ^3He has two protons and one neutron in its nucleus, and ^4He has two protons and two neutrons in its nucleus.

The isotopic ratio of helium in a sample can be expressed as $\delta^3\text{He}$ in units of percent:

$$\delta^3\text{He} = \left[\frac{(^3\text{He} / ^4\text{He})_{\text{sample}}}{(^3\text{He} / ^4\text{He})_{\text{air}}} - 1 \right] \times 100$$

A tritium unit (TU) is equal to 3.19 picocuries per liter.

Concentrations of gases in water are given in several units:

pptv, volume of gas per volume of dry air, in parts per trillion.

mmol/L, millimoles of gas per liter of water.

mmol/kg, millimoles of gas per kilogram of water.

$\mu\text{mol/L}$, micromoles of gas per liter of water.

nmol/kg, nanomoles of gas per kilogram of water.

pmol/kg, picomoles of gas per kilogram of water.

fmol/kg, femtomoles of gas per kilogram of water.

mg/L, milligrams of gas per liter of water.

cm^3/g or cc/g , cubic centimeters of gas at standard temperature and pressure (STP) per gram of water.

cm^3/kg , cubic centimeters of gas at standard temperature and pressure per kilogram of water.

Abbreviations

AEW	Air-equilibrated distilled water
CE	Closed-system equilibration
F	Fractionation
ID	Identification
PR	Partial re-equilibration
T	Temperature
UA	Unfractionated excess air
USGS	U.S. Geological Survey

CHEMICAL NAMES

^3H	Tritium
$^3\text{He}_{\text{trit}}$	Tritogenic helium-3
$^4\text{He}_{\text{rad}}$	Radiogenic helium-4
Ar	Argon
CFC-11	Trichlorofluoromethane (chlorofluorocarbon-11)
CFC-113	1,1,2-Trichloro-1,2,2-trifluoroethane (chlorofluorocarbon-113)
CFC-12	Dichlorodifluoromethane (chlorofluorocarbon-12)
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
$\delta^3\text{He}$	delta helium-3
H_2	Hydrogen
Halon-1301	Bromotrifluoromethane
He	Helium
He_a	Helium originating from excess air
He_{eq}	Helium in solubility equilibrium with the atmosphere
He_s	Measured total dissolved helium
He_{terr}	Terrigenous helium
Kr	Krypton
N	Nitrogen
N_2	Nitrogen gas
N_2O	Nitrous oxide
NaCl	Sodium chloride
Ne	Neon
O_2	Oxygen
R_a	$^3\text{He}/^4\text{He}$ atom ratio of the atmosphere
R_{eq}	Isotopic fractionation of helium during air-water solubility equilibrium
R_s	Measured $^3\text{He}/^4\text{He}$ atom ratio of the sample
R_{terr}	$^3\text{He}/^4\text{He}$ atom ratio of the terrigenous helium
SF_6	Sulfur hexafluoride
Xe	Xenon

DGMETA (Version 1): Dissolved Gas Modeling and Environmental Tracer Analysis Computer Program

By Bryant C. Jurgens¹, J.K. Böhlke², Karl Haase², Eurybiades Busenberg², Andrew G. Hunt³, and Jeffrey A. Hansen¹

Abstract

DGMETA (Dissolved Gas Modeling and Environmental Tracer Analysis) is a Microsoft Excel-based computer program that is used for modeling air-water equilibrium conditions from measurements of dissolved gases and for computing concentrations of environmental tracers that rely on air-water equilibrium model results. DGMETA can solve for the temperature, salinity, excess air, fractionation of gases, or pressure/elevation of water when it is equilibrated with the atmosphere. Models are calibrated inversely using one or more measurements of dissolved gases such as helium, neon, argon, krypton, xenon, and nitrogen. Excess nitrogen gas, originating from denitrification or other sources, also can be included as a fitted parameter or as a separate calculation from the dissolved gas modeling results. DGMETA uses the air-water equilibrium models to separate measured concentrations of gases and isotopes of gases into components that are used for tracing water in the environment. DGMETA calculates atmospheric dry-air mole fractions (mixing ratios) for transient atmospheric gas tracers such as chlorofluorocarbons, sulfur hexafluoride, and bromotrifluoromethane (Halon-1301); and concentrations of tritiogenic helium-3 and radiogenic helium-4, which accumulate from the decay of tritium in water and the decay of uranium and thorium in rocks, respectively.

Sample data can be graphed to identify applicable models of excess air, samples that contain excess nitrogen gas, or samples that have partially degassed, for example. Monte Carlo analysis of errors associated with dissolved gas equilibrium model results can be carried through computations of environmental tracer concentrations to provide robust estimates of error. In addition, graphical routines for separating helium sources using helium isotopes are included to refine estimates of tritiogenic helium-3 when terrigenous helium from mantle or crustal sources is present

in samples. Environmental tracer concentrations and their errors computed from DGMETA can be used with other programs, such as TracerLPM (Jurgens and others, 2012), to determine groundwater ages and biogeochemical reaction rates. DGMETA also produces output files in a format that meets the U.S. Geological Survey open data requirements for documentation of model inputs and outputs.

DGMETA is a versatile and adaptable program that allows users to add solubility data for new gases, modify the existing set of gas solubility data, modify the default set of gases used for modeling, choose calculations based on real (non-ideal) gas behavior, and select various concentration units for data entry and results to match laboratory reports and study objectives. DGMETA comes with a set of gases widely used in hydrology and oceanography and many gases include multiple solubilities from previous work. Seventeen dissolved gases are included in the default version of the program: noble gases (helium, neon, argon, krypton, and xenon), reactive gases (nitrogen, oxygen, methane, carbon dioxide, carbon monoxide, hydrogen, and nitrous oxide), and environmental tracers (chlorofluorocarbon-11, chlorofluorocarbon-12, chlorofluorocarbon-113, sulfur hexafluoride, and Halon-1301).

Introduction

Analysis of dissolved gases in water is common in oceanographic and terrestrial hydrologic studies. Various combinations of dissolved gases can provide records of environmental change and a deeper understanding of groundwater flow systems (Heaton and Vogel, 1981; Heaton and others, 1983; Stute and others, 1995; Aeschbach-Hertig and others, 1999; Ballentine and Hall, 1999; Cey and others, 2008; Cartwright and others, 2017), groundwater discharges to surface water (Heilweil and others, 2015; Sanford and others, 2015; Gilmore and others, 2016), ocean circulation patterns and mixing (Schlosser and Winckler, 2002; Stanley and Jenkins, 2013; Loose and Jenkins, 2014), and emission rates of greenhouse gases from parts of the hydrosphere (Matthews and Fung, 1987; Dalal and Allen, 2008; Jeffrey and others, 2018).

¹U.S. Geological Survey, Placer Hall, 6000 J St., Sacramento, CA 95819, bjurgens@usgs.gov

²U.S. Geological Survey, 431 National Center, Reston, VA 20192

³U.S. Geological Survey, Denver Federal Center, Lakewood, CO, 80225

2 DGMETA (v.1): Dissolved Gas Modeling and Environmental Tracer Analysis Computer Program

Dissolved gases with constant atmospheric abundances like the inert noble gases helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe; [fig. 1A](#)) or the reactive gas nitrogen (N_2 ; [fig. 1B](#)) are commonly used to evaluate the conditions (temperature or excess air, for example) of water when it is equilibrated with the atmosphere. Reactive gases such as N_2 , oxygen (O_2), carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), hydrogen (H_2), and nitrous oxide (N_2O ; [fig. 1B](#)) can be used to evaluate biogeochemical processes. Relatively stable, but transient (time-varying) atmospheric trace gases like sulfur hexafluoride (SF_6), chlorofluorocarbon-11 (CFC-11), chlorofluorocarbon-12 (CFC-12), chlorofluorocarbon-113 (CFC-113), and bromotrifluoromethane (Halon-1301) are commonly used to trace water in the environment ([fig. 1C](#)). Transient atmospheric gases and the isotopes of helium (helium-3/helium-4, $^3He/^4He$; or the delta helium-3, δ^3He)—tritogenic helium-3 ($^3He_{trit}$) and radiogenic helium-4 ($^4He_{rad}$)—are commonly known as “environmental tracers” and are frequently used to evaluate residence times of water and groundwater. Tritogenic helium-3 can accumulate in water from the decay of tritium (3H) in water and $^4He_{rad}$ can accumulate in water from uranium and thorium in subsurface rocks.

The measured concentrations of reactive gases, transient atmospheric gases, and He with He isotopes are not typically meaningful because the concentration that was gained or lost from biogeochemical reactions or the concentration used for age-dating water, like the dry-air mole fraction or the amount of He produced from the decay of tritium ($^3He_{trit}$), are calculated quantities that are dependent on the air-water equilibration conditions when the water was last in contact with the atmosphere. The air-water equilibration conditions such as temperature and excess air contribution may be estimated or, more frequently, they are determined by inverse modeling of noble gases or Ar- N_2 . Consequently, samples for the noble gases (with He isotopes), reactive gases, and transient atmospheric tracers are increasingly collected together to gain a more complete analysis of gases in water.

Different sets of dissolved gases commonly are sampled in separate containers, analyzed at different laboratories, and may be interpreted separately using software programs available publicly, in literature, or provided by the laboratories. Noble90 (Aeschbach-Hertig and others, 1999, 2000; Peeters and others, 2003), NOBLEBOOK (Aeschbach-Hertig and others, 1999, 2000), and PANGA (Jung and Aeschbach-Hertig, 2018) are programs available for modeling air-water equilibrium conditions from noble gases. Noble90 also can be used to calculate He components from model results. These programs rely on a limited set of gas solubility equations that are widely used but cannot be

changed or updated without a substantial alteration of the program. In addition, no single program is available that can compute a wide range of commonly sampled environmental tracers, such as CFCs, SF_6 , and Halon-1301, or provide a way to interactively compute He components ($^3He_{trit}$, $^4He_{rad}$) in the context of local conditions through graphical inspection and manipulation of dependent terms. Because environmental tracer interpretations are dependent on dissolved gas model results, and different combinations of gases may be included in various studies, a single program that is capable of simultaneously and consistently interpreting the full range of dissolved gases and environmental tracers is desirable.

The purpose of this report is to document the program DGMETA: Dissolved Gas Modeling and Environmental Tracer Analysis is a Microsoft Excel-based program that is compatible with Excel Office versions 2007 or later. DGMETA can be used for inverse modeling of air-water equilibrium conditions (temperature, excess air, gas fractionation, and pressure/elevation) from stable atmospheric dissolved gases (He, Ne, Ar, Kr, Xe, and N_2); for evaluating environmental tracers of relatively stable, but transient atmospheric trace gases (such as the CFCs, SF_6 , and Halon-1301); and for evaluating environmental tracers produced within the subsurface from the decay of tritium in water, like $^3He_{trit}$, or from the decay of uranium and thorium in rocks such as $^4He_{rad}$. DGMETA can be used to model air-water equilibrium conditions assuming that excess air is unfractionated (UA; Heaton and Vogel, 1981), fractionated following the partial re-equilibration model (PR; Stute and others, 1995) of excess air, or fractionated following the closed-system equilibration model (CE; Aeschbach-Hertig and others, 2000) of entrapped air. Gases that are transient or biologically reactive also are included. These gases can be used to identify O_2 and nitrate reduction, CH_4 production, and other biogeochemical processes. Finally, DGMETA has the added capability for users to modify or add to the set of gas solubility equations included in DGMETA's solubility database, including atmospheric gas tracers. These modifications allow DGMETA to grow as new tracers are identified or as solubility equations are revised.

This report contains three sections: Methods, Program Description, and Examples. The “Methods” section describes the theoretical and empirical basis for the dissolved gas and tracer models and the computational methods used by DGMETA. The “Program Description” section describes the contents of the worksheets in DGMETA, the input data required for operation of the software, and how to use the functions provided in the DGMETA Excel ribbon. The “Examples” section includes five examples of using DGMETA to process dissolved gas data of different types.

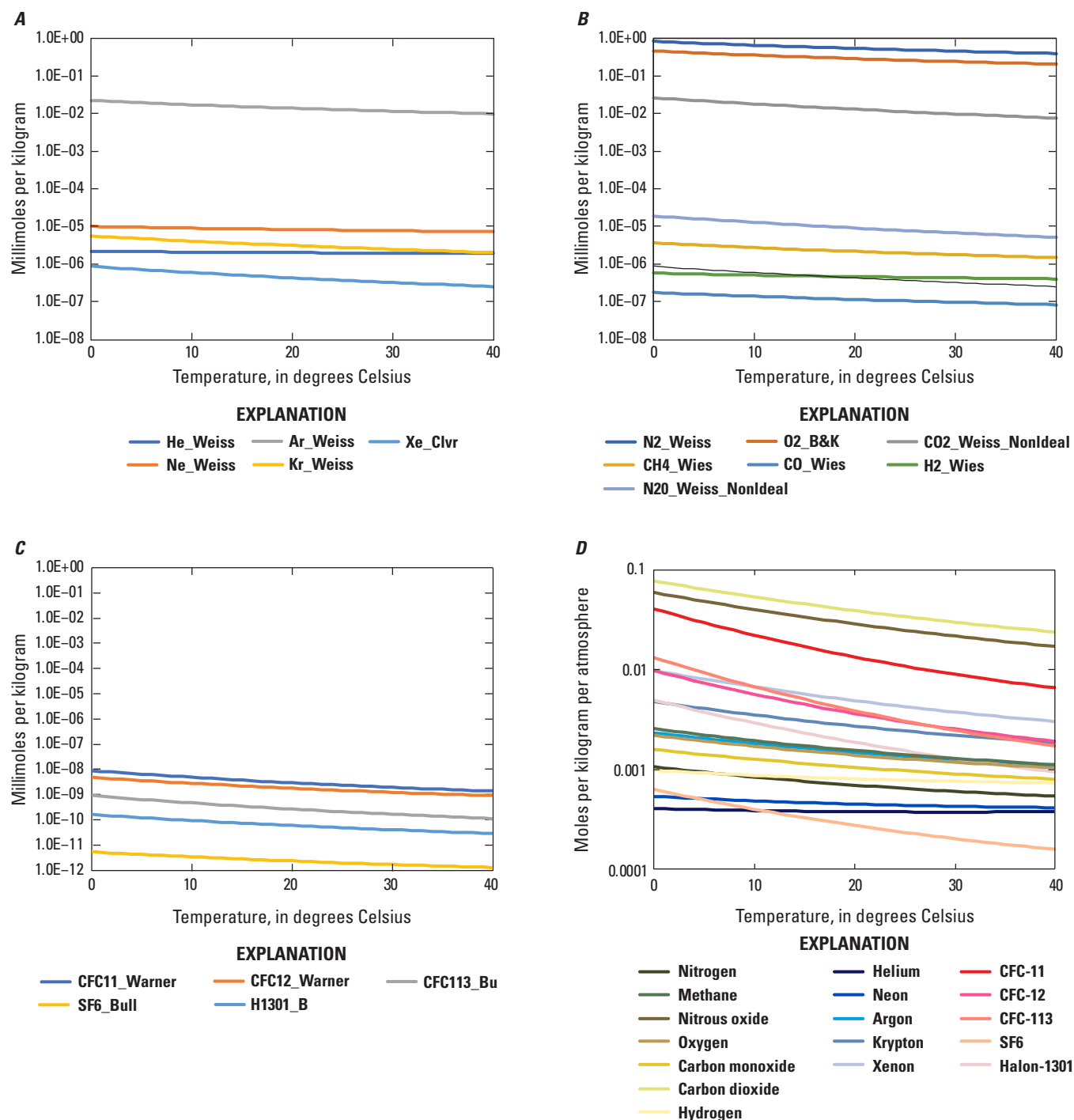


Figure 1. *A*, air-water solubility equilibrium concentration of inert (non-reactive) noble gases helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) in water that are commonly used for modeling air-water equilibrium conditions; *B*, air-water solubility equilibrium concentration of the biogeochemically reactive gases nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), methane (CH_4), carbon monoxide (CO), hydrogen (H_2), and nitrous oxide (N_2O); *C*, air-water solubility equilibrium concentration of environmental tracers chlorofluorocarbon-11, -12, -113 (CFC-11, CFC-12, CFC-113), sulfur hexafluoride (SF_6), and bromotrifluoromethane (halon-1301) that are commonly used for determining residence times of water; and *D*, Henry solubility constant of noble gases, reactive gases, and environmental tracers. Solubility concentration of the gases were determined for freshwater (salinity = 0 per mil) over the temperature range of 0–40 degrees Celsius at sea level (atmospheric pressure = 1 standard atmosphere). The names of the lines consist of the name of the gas and a descriptor of the reference for the sources of the gas solubility data; and they are unique identifiers for the gas solubility data used by Dissolved Gas Modeling and Environmental Tracer Analysis (DGMETA; see the Database worksheet of DGMETA).

Methods

The dissolved concentration of a gas, C_t , in water includes three major components: (1) the concentration of dissolved gas attributable to its solubility equilibrium with the atmosphere, C_{eq} ; (2) an amount of gas in excess of solubility equilibrium resulting from the dissolution of air bubbles, C_a ; and (3) an amount of gas that is produced or consumed in situ, either in an ocean, aquifer, surface water, or streambed, C_{is} .

$$C_t = C_{eq} + C_a + C_{is} \quad (1)$$

For some gases, the in situ production in water is zero or negligible. For other gases, the in situ production may be from biological processes (N_2 ; Heaton and others, 1983), radioactive decay of aquifer materials ($^4He_{rad}$; Andrews and Lee, 1979), the decay of tritium in water ($^3He_{trit}$; Tolstikhin and Kamensky, 1969), or upwards migration of deep crustal or mantle fluids (Craig and others, 1978). Some gases can be consumed by biological processes that result in negative in situ concentration (for example, O_2 reduction). Because the noble gases (He, Ne, Ar, Kr, and Xe) are chemically non-reactive, have stable concentrations in the atmosphere, and (except for He) have in situ production rates that are often negligible, they provide the best tool for determining the temperature and excess air component of water when it equilibrated with the atmosphere (Kipfer and others, 2002).

Relatively stable, transient atmospheric trace gases, such as CFCs, SF_6 , and Halon-1301, are often used to determine the residence time of reservoirs of water because their concentrations in the atmosphere have changed since the 1930s (Gammon and others, 1982; Bullister and Weiss, 1983; Bullister, 1984; Bullister and Weiss, 1988; Busenberg and Plummer, 1992; Bu and Warner, 1995; Busenberg and Plummer, 2000; Bullister and others, 2002; Deeds, 2008; Beyer and others, 2014, 2015, 2017). To determine residence time, it is necessary to compute the atmospheric mole fraction (of dry air) of the gas when the water equilibrated with the atmosphere. Because the air-water equilibrium conditions are often unknown, it is common to measure noble gases (and nitrogen; N) along with CFCs, SF_6 , or Halon-1301 to provide the best estimate of air-water equilibrium conditions. The dry-air mole fraction of a CFC, SF_6 , or Halon-1301 in water can be compared to the time-varying record of dry-air mole fractions in the atmospheric record to determine the year or range of years in which the water could have entered a reservoir of water. These methods also can apply to other more chemically reactive gases or transient gases to understand reaction rates and climate change records or deviations from non-equilibrium conditions.

Gas Solubilities

The solubility equilibrium concentration of a gas in water, C_{eq} , is governed by Henry's law, which says that the concentration of a gas dissolved in water is proportional to the partial pressure of the gas, p , above the water; this proportional relationship is defined as the Henry solubility constant: $K_{cp} = \frac{C_{eq}}{p}$ (commonly referred to as "K"). Henry's law also is frequently defined as a volatility constant, K_{pc} (commonly known as " K_H "), which is the inverse of K_{cp} or $K_{pc} = 1 / K_{cp}$; as this name implies, it is often used for expressing the volatility of sparsely soluble organic compounds from water. Henry's law also can be defined as a dimensionless molar ratio, H , that represents the molar concentration of the gas in water to the molar concentration of the gas in air. The Henry solubility constant, volatility constant, and dimensionless Henry constant are related by $H = RTK_{cp} = RT/K_{pc}$, where R is the universal gas constant [82.056 cubic centimeters (cm^3)-atm per mol per Kelvin] and T is the temperature in Kelvin. For solubility studies of the atmospheric gases, the Henry solubility constant, K_{cp} , is the most commonly used form of Henry's law, and this form is adopted by DGMETA.

The concentration of a dissolved gas in equilibrium with the atmosphere is calculated using the following formula:

$$C_{eq} = x(P_h - e_w)G_{(T,S)} \times \text{correction factors} \quad (2)$$

where

- C_{eq} is the solubility concentration in equilibrium with the atmosphere and may be computed in volumetric (cm^3/g), mass (milligrams per liter; mg/L), molar (millimole per L; mmol/L), or molal (mmol/kilogram; kg) concentration units,
- x is the dry-air mole fraction of the gas in the atmosphere in mole fraction,
- P_h is the local total atmospheric pressure in atm,
- e_w is the water vapor pressure (or saturation vapor pressure of water) in atm,
- $G_{(T,S)}$ is the generalized Henry solubility constant of a gas in water and is a function of temperature, T , and salinity, S , and may be expressed in any concentration units per atm,
- T is the temperature of water in Kelvin,
- S is the salinity of water in parts per thousand (per mil) or g per kg (equivalent to 1 part dissolved solute per 1,000 parts of water), and
- correction factors* (for example, P_c , R_c , U_C , are defined in equations 7–12) are used as needed, depending on the form and units of $G_{(S,T)}$.

Equation 2 is the general equation used by the program for computing the solubility of a gas in water and it is a function of the partial pressure of a gas [$x(P_h - e_w)$] and the solubility function $G_{(T,S)}$. As written, $G_{(T,S)}$ is equal to the Henry's law solubility constant, K_{cp} , and is a function of temperature and salinity in any concentration units per atm. Equation 2 has been generalized to account for different definitions, formulations, and units of the solubility function, $G_{(T,S)}$, that was derived in the original solubility study of a gas. DGMETA builds specific forms of equation 2 in a modular fashion, such that the dry-air mole fraction, correction factors, and conversion terms can be added or removed based on the form of the solubility function, $G_{(T,S)}$. By default, DGMETA converts all gas concentrations to cm³/g of water—see the “Unit Conversions” section below. For gases that have transient dry-air mole fractions (x), the equilibrium concentration of the gas will depend on the year in which the water was last in contact with the atmosphere. For such gases, the dry-air mole fractions can be manually adjusted from the Database worksheet by entering a different mole fraction from the atmospheric record for a particular year of interest.

DGMETA includes solubility equations for several gases: He, Ne, Ar, Kr, Xe, N₂, CO₂, H₂, O₂, CH₄, N₂O, CO, CFC-11, CFC-12, CFC-113, SF₆, and Halon-1301. This list can be expanded to suit user needs by entering gas solubility data and properties into the Database worksheet. The solubility equations were primarily derived to compute gas concentrations in fresh water and seawater over the salinity range of 0–35 per mil (‰ or g/kg), temperature range of 0–40 degrees Celsius (°C), and pressure range of 0.5–1.0 atm, which corresponds to altitudes between sea level (1 atm) and 6,000 meters (m) above sea level, approximately.

Approximations for Local Pressure, Water Vapor Pressure, and Salinity

DGMETA uses the U.S. Standard Atmosphere (National Aeronautics and Space Administration, 1976) and barometric formula to approximate local atmospheric pressure based on an elevation specified by the user. The elevation may be based on the site location or the elevation where water enters an aquifer as recharge. DGMETA calculates pressure for the base level U.S. Standard Atmosphere only. The following calculation is valid for elevations less than 11,000 m:

$$P_h = P_o \left[\frac{T_b}{T_b + L_b (h - h_0)} \right]^{\frac{g_0 M_a}{R^* L_b}} \quad (3)$$

where

- P_h is the local atmospheric pressure in atm,
- P_o is the sea level standard atmospheric pressure in atm (1 atm = 1013.25 millibars),
- T_b is the standard temperature, 288.15 Kelvin,
- L_b is the standard lapse rate, -0.0065 Kelvin per m,
- h is the elevation in m above sea level,
- h_0 is the elevation of the bottom layer, 0 m above sea level,
- g_0 is the gravitational acceleration, 9.80665 m per second squared,
- M_a is the molar mass of air, 0.0289644 kg per mol, and
- R^* is the universal gas constant, defined as 8.3144598 joules (J) per mol per Kelvin by the U.S. Standard Atmosphere.

DGMETA approximates the water vapor pressure using the equation from Weiss and Price (1980):

$$e_w = \exp \left[24.4543 - \frac{6745.09}{T} - 4.8489 \ln \left(\frac{T}{100} \right) - 0.000544S \right] \quad (4)$$

where

- e_w is the water vapor pressure (or saturation vapor pressure of water) in atm,
- T is the temperature of water in Kelvin, and
- S is salinity in per mil or g/kg.

When direct measurements of salinity or total dissolved solids are not available, salinity, S , can be approximated from measurements of specific conductance (SC) using an equation taken from Pickering (1981):

$$S(\text{permilorg/kg}) = 5.572 \times 10^{-4}(SC) + 2.02 \times 10^{-9}(SC)^2 \quad (5)$$

where

- S is salinity in per mil or g/kg, and
- SC is the specific conductance in microsiemens per centimeter ($\mu\text{S/cm}$).

Salinity is dependent on the ionic composition of water; therefore, relations between S and SC can vary for different environmental settings. Equation 5 was derived from more complex equations published in Standard Methods (American Public Health Association, 2005) with the assumption that the dissolved ions in water are identical to those in seawater. Differences between the predictions of equation 5 and the equations from Standard Methods typically result in less than a 0.1 percent change in the salinity factor over a wide range of temperature (0–40 °C) and specific conductance (0–67,000 $\mu\text{S}/\text{cm}$) values (U.S. Geological Survey, 2011). Consequently, this equation provides a reasonable approximation for most study objectives and applications.

Forms of Solubility Equations

As written in equation 2, $G_{(T,S)}$ is equal to the Henry's law solubility constant, K_{cp} , and is a function of temperature and pressure and is usually expressed in volumetric or gravimetric concentrations per atm. Equation 2 has been generalized to account for different definitions, formulations, and units of the solubility function, $G_{(T,S)}$, that was derived in the original solubility study of a gas. In general, two forms of $G_{(T,S)}$ are most often used for reporting solubility results. In one form, $G_{(T,S)}$ is a function for the solubility constant (K_{cp}), Bunsen solubility constant (β ; Weiss, 1970), mole fraction (X ; Clever, 1979a; Smith and Kennedy, 1983), solubility constants that require a modified form of equation 2 for real gas behavior, such as K_o (Weiss, 1974; Weiss and Price, 1980), or that approximate real gas behavior at pressures near 1 atm, such as K' (Warner and Weiss, 1985; Bu and Warner, 1995). In these cases, the corrections applied to equation 2 may only require conversion to different units—see the “Unit Conversions” section or correction for real gas behavior. The other form of $G_{(T,S)}$ that is frequently used is the moist-air solubility, which is the volume or concentration of a gas in water at equilibrium with water saturated air at a total pressure of 1 atm. In other words, this is the volume or concentration of a gas expected to be dissolved in seawater or freshwater at sea level. This form is noted as C^* (Weiss, 1970) and it includes the partial pressure of the gas at sea level in the solubility expression $[x(P_0 - e_w)]$. It is, therefore, necessary to remove the pressure term from equation 2 to compute the solubility concentration at other elevations (or pressures)—see the “Correction” sections below. Similar to C^* , Weiss and Price (1980) and Benson and Krause (1984) derived equations that included the effects of real gas behavior for moist-air solubility concentrations in seawater or freshwater at sea level. To use their equations in equation 2, the pressure terms and non-ideality terms at 1 atm must be corrected in order to compute the solubility concentration at other elevations (pressure)—see the “Correction” sections below.

The solubility function, $G_{(T,S)}$, is usually a two- or three-part polynomial with coefficients that express the temperature and salinity dependence of the gas in water at 1 atm. Most often the solubility equation is based on the integrated van 't Hoff equation and the Setchénow relation for salinity. The coefficients of the polynomial are found by fitting experimental solubility data to the function. The concentration units of $G_{(T,S)}$ are, therefore, dependent on the concentrations used in the experiment. DGMETA accepts most concentration units expressed as volumetric, gravimetric, molar, or molal units per atm. DGMETA will convert the concentrations internally to a common unit of cm^3/g and can output concentrations in either cm^3/g , mmol/L , mmol/kg , or mg/L —see the “Unit Conversions” section.

Below is a list of solubility equations that can be used to compute dissolved gas concentrations in water:

$$\ln C^* \text{ or } \ln \beta = A_1 + A_2 \left(\frac{100}{T} \right) + A_3 \ln \left(\frac{T}{100} \right) + A_4 \left(\frac{T}{100} \right) + S \left[B_1 + B_2 \left(\frac{T}{100} \right) + B_3 \left(\frac{T}{100} \right)^2 \right] \quad (\text{G}_1)$$

$$\ln K_o, \ln K', \text{ or } \ln F^* = A_1 + A_2 \left(\frac{100}{T} \right) + A_3 \ln \left(\frac{T}{100} \right) + A_4 \left(\frac{T}{100} \right)^2 + S \left[B_1 + B_2 \left(\frac{T}{100} \right) + B_3 \left(\frac{T}{100} \right)^2 \right] \quad (\text{G}_2)$$

$$\ln X = A_1 + A_2 \left(\frac{100}{T} \right) + A_3 \ln \left(\frac{T}{100} \right) - NaCl \left[B_1 + B_2 \left(\frac{100}{T} \right) + B_3 \ln \left(\frac{T}{100} \right)^2 \right] \quad (\text{G}_3)$$

$$\ln C^* = A_1 + \frac{A_2}{T} + \frac{A_3}{T^2} + \frac{A_4}{T^3} + \frac{A_5}{T^4} + S \left[B_1 + \frac{B_2}{T} + \frac{B_3}{T^2} \right] \quad (\text{G}_4)$$

$$\ln C^* = A_1 + \frac{A_2}{T_s} + \frac{A_3}{T_s^2} + \frac{A_4}{T_s^3} + \frac{A_5}{T_s^4} + \frac{A_6}{T_s^5} + S \left[B_1 + \frac{B_2}{T_s} + \frac{B_3}{T_s^2} + \frac{B_4}{T_s^3} \right] + C_1 S^2 \quad (\text{G}_5)$$

$$\ln C^* = A_1 + A_2 \left(\frac{100}{T} \right) + A_3 \ln \left(\frac{T}{100} \right) + A_4 \left(\frac{T}{100} \right) + S \left[B_1 + B_2 \left(\frac{T}{100} \right) + B_3 \left(\frac{T}{100} \right)^2 \right] + C_1 S^2 \quad (\text{G}_6)$$

where

- \ln is the natural logarithm, a logarithm to base e (a mathematical constant approximated as 2.71828),
- C^* is the moist-air solubility concentration and is the volume or concentration of a gas in water at equilibrium with water saturated air at a total pressure of 1 atm,
- β is the Bunsen coefficient and is the volume of gas at standard temperature and pressure (STP) that partitions into the aqueous phase per unit volume of water at the temperature of the measurement when the partial pressure of the gas is 1 atm in milliliters (mL) of gas per L of water,
- A_j is the gas temperature coefficient for the j -th term (1–6),
- B_j is the gas salinity coefficient for the j -th term (1–4),
- C_l is the gas salinity coefficient for certain formulations,
- S is the salinity of the water in per mil or g/kg,
- T is the water temperature in Kelvin for equations G_1 , G_2 , G_3 , and G_6 ,
- T_s is the scaled temperature of water, unitless, for equations G_4 and G_5 , calculated as $\ln\left(\frac{298.15-t}{273.15+t}\right)$, where t is temperature in $^{\circ}\text{C}$,
- K_o is the fugacity solubility constant in mol per kg per atm (Weiss and Price, 1980; Warner and Weiss, 1985),
- K' is the partial pressure equilibrium solubility constant in mol per kg of water per atm (Warner and Weiss, 1985),
- F^* is moist-air solubility concentration adjusted for real gas behavior (Weiss and Price, 1980; Warner and Weiss, 1985),
- X is the mole fraction solubility concentration (Clever 1979a, b, 1980; Smith and Kennedy, 1983), and
- $NaCl$ is the sodium chloride concentration in mol per L and is calculated following Aeschbach-Hertig and others (1999) as [equation 6](#) below.

$$NaCl = \frac{S}{M_{NaCl}} \rho_{(t,S)} / 1000 \quad (6)$$

where

- M_{NaCl} is the molar mass of sodium chloride, 58.443 g/mol, and

- $\rho_{(t,S)}$ is the density of water as function of temperature and salinity in kg per cubic meter (m^3)—see the “Unit Conversions” section for the calculation.

Equation G_1 was used by Weiss (1970, 1971) to compute solubilities for dissolved N, O₂, and Ar (Weiss, 1970), for He and Ne (Weiss, 1971), and for CH₄, CO, and H₂ (Wiesenburg and Guinasso, 1979) in fresh water and seawater. This equation is formulated with the integrated van 't Hoff equation for temperature and the Setchénow relation for salinity and can be used to compute gas solubilities from Bunsen constants (β) or as moist air solubilities (C^*). Weiss and Price (1980) used equation G_2 to compute the fugacity solubility coefficient (K_o) and fugacity adjusted moist-air solubility (F^*) for N₂O and CO₂. Equation G_3 is from Clever (1979a, b) and Smith and Kennedy (1983) and was used to compute solubilities of the noble gases in fresh water and seawater. Equation G_4 was used by Benson and Krause (1984) to compute dissolved O₂ concentrations in fresh water and seawater. Equation G_5 was used by Garcia and Gordon (1992, 1993) to compute dissolved O₂ solubility and later was used by Hamme and Emerson (2004) for Ne, Ar, and N in fresh water and seawater. Equation G_6 was used by Jenkins and others (2019) to fit noble gas solubility data in water and seawater.

Pressure Corrections

Some expressions of gas solubility were derived for moist air at sea level (total pressure is 1 atm, adjusted for water saturated air) to facilitate use in oceanographic studies. These solubility forms are often noted as C^* or F^* (eqs. G_1 , G_4 , G_5 , and G_6), and these forms need pressure corrections to be used at other elevations (pressures; Benson and Krause, 1984; Kipfer and others, 2002). DGMETA will apply the following correction term when the value of the “Use pressure correction, P_c ” field is “Yes” on the Database worksheet:

$$P_c = \frac{1}{P_o - e_w} \quad (7)$$

where

- P_c is an optional pressure correction for water vapor when the solubility constant $G_{(S,T)}$ is normalized to moist air at 1 atm,
- P_o is the sea level standard atmospheric pressure in atm (1 atm = 1013.25 millibars), and
- e_w is the water vapor pressure (or saturation vapor pressure of water) in atm.

Real Gas Corrections

Two methods for dealing with non-ideal behavior of real gases are included in the program. DGMETA will compute additional gas corrections for non-ideal behavior when the value in the “Treat non-ideal” field is “Yes” on the Database worksheet. Some gases can deviate from ideal behavior, and these deviations may limit the accuracy of the solubility computations. For many gases this deviation is small at total pressures near 1 atm in comparison to solubility measurements (Weiss and Price, 1980; Warner and Weiss, 1985). Benson and others (1979) and Benson and Krause (1984) used the second virial coefficient to correct O₂ for real gas behavior. Similarly, Weiss and Price (1980) derived a relationship for the second virial and cross virial coefficient to correct N₂O and CO₂ for real gas behavior:

Benson and others (1979) and Benson and Krause (1984):

$$R_c = \frac{1 - \theta P_h}{1 - \theta} \quad (8)$$

where

- R_c is the local real gas correction, in atm,
- θ is a polynomial function for the second virial coefficient between oxygen and air (eq. 22 in Benson and others, 1979), and
- P_h is the local atmospheric pressure in atm.

Weiss and Price (1980):

$$R_c = \exp \left[P_h \left(\frac{B + 2\delta}{RT} \right) + \bar{v} \left(\frac{1 - P_h}{RT} \right) \right] = \exp \left[P_h B^* + \bar{v} \left(\frac{1 - P_h}{RT} \right) \right] \quad (9)$$

where

- R_c is the real gas correction,
- P_h is the local atmospheric pressure in atm,
- B^* is a polynomial function (eq. 11 in Weiss and Price, 1980) relating the quantity $\frac{B + 2\delta}{RT}$, where B is the second virial coefficient and δ is the cross-virial coefficient between the trace gas and air,
- \bar{v} is the partial molal volume in cm³ per mol,
- R is the gas constant (82.056 cm³-atm per mol per Kelvin), and
- T is the temperature in Kelvin.

For CO₂, Weiss (1974) did not define the expansion series, B^* , like was done for N₂O (Weiss and Price, 1980). To facilitate the use of equation 9 with CO₂, the function B^* (eq. 11 in Weiss and Price, 1980) was fitted to the quantity $\frac{B + 2\delta}{RT}$ based on equations for the second virial coefficient and cross-virial coefficient given by Weiss (1974). For formulations in moist air at sea level, F^* , the real gas correction at sea level must be removed to apply it at other

elevations. This is done by dividing the real gas correction (eq. 9) by the real gas correction at sea level, $\exp(B^*)$.

Unit Conversions

Solubilities can be reported in gravimetric, volumetric, molar, or molal concentration units or mole fractions, X . By default, DGMETA automatically converts all gas solubilities internally from the units specified in the “Units of solubility constants” field on the Database worksheet to cubic centimeters of gas at an STP per gram of water, which is the most common unit of measurement of the noble gases. Most units can be converted using the density of water, molar gas volume, and molar mass of each gas. In general, conversion to and from cubic centimeters per gram use the molar volumes of each gas defined on the Database worksheet rather than the molar volume of an ideal gas ($M_I = RT \approx 22.414$). The default molar volumes are computed by dividing the molar mass by the molar density. It is possible that the original solubility study used M_I for conversions, and therefore, in some cases the M_I may be more appropriate than the individual molar gas volumes used by default. Solubilities as mole fractions (Clever, 1979a, b, 1980; Smith and Kennedy, 1983) are converted to cubic centimeters per gram following Aeschbach-Hertig and others (1999). All dissolved gas modeling results report gas concentrations of each model component in cm³/g, mmol/L, and mg/L:mmol/L to cm³/g:

$$U_c = \frac{V}{\rho_{(t,S)}} \quad (10)$$

mg/L to cm³/g:

$$U_c = \frac{V}{M\rho_{(t,S)}} \quad (11)$$

mole fraction to cm³/g:

$$U_c = \frac{V}{M_{H_2O}} \left(\frac{X}{1-X} \right)^{\rho_{(t,S)}^0} \quad (12)$$

Bunsen solubility (cm³/mL) to cm³/g:

$$U_c = \frac{1}{\rho_{(t,S)}} \quad (13)$$

where

- V is the molar volume of a gas in mols per cm³ (molar mass in g/mol divided by molar density in g/cm³),
- $\rho_{(t,S)}$ is the density of water as function of temperature and salinity in kg/m³—see the “Unit Conversions” section for the calculation,
- M is the molar mass of a gas in g per mol,
- X is the mole fraction of a gas in water, in mol of gas per mol of water, and
- M_{H_2O} is the molar mass of water (18.016 g per mol).

The density of water, $\rho_{(t,S)}$, in kg per cubic meter (m^3), is computed from the equations derived by Bigg (1967a, b) and Millero and Poisson (1981). It is computed in two parts:

$$\rho_{(t,S)} = \rho_{(t)} + AS + BS^{\frac{3}{2}} + CS \quad (14)$$

where

$$\rho_{(t)} = 999.842594 + 6.793952 \times 10^{-2}t - 9.09529 \times 10^{-3}t^2 + 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + 6.536336 \times 10^{-9}t^5$$

Bigg (1967a, b):

$$\begin{aligned} A &= 0.824493 - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4 \\ B &= -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.66546 \times 10^{-6}t^2 \\ C &= 4.8314 \times 10^{-4} \\ S &\text{ is the salinity of the water in per mil or g/kg,} \\ t &\text{ is the temperature in } ^\circ\text{C.} \end{aligned}$$

Models of Excess Air

DGMETA can be used to model air-water equilibrium conditions under different theories of the presence and partitioning of excess air, represented as C_a in [equation 1](#). Excess air (A) is a phenomenon in which dissolved gas concentrations exceed the concentrations attributable to equilibrium in the atmosphere (Heaton and Vogel, 1981). The composition of the excess air is similar to the composition of the atmosphere, hence the name “excess air.” This extra amount of air is from air-bubbles entrained in water that may be partially or completely dissolved into solution. Excess air may form in groundwater from water-table fluctuations during recharge or in ocean and surface-water bodies from wave action.

Dissolved gas concentrations of excess air can be unfractionated or fractionated relative to the atmospheric composition. Excess air will be unfractionated (UA) when air bubbles are completely dissolved into a solution (Heaton and Vogel, 1981; [eq. 15](#)). Fractionated excess air can occur from the diffusion of gases across a water table or by incomplete dissolution of entrapped air bubbles (A_e). Stute and others (1995) proposed a partial re-equilibration (PR) model of fractionated excess air that describes a process where water loses its excess air component through progressive re-equilibration with the atmosphere via diffusion of gases across a water table or water surface ([eq. 16](#)). Because lighter gases will diffuse more quickly than heavier ones, the water is depleted in lighter gases relative to the heavier gases. The fractionation parameter, F , used in the PR model is the degree to which the gases have fractionated and may range from zero (unfractionated amount of excess air) to infinity (zero excess air). Excess air also can be fractionated if entrapped air-bubbles are only partially dissolved into a solution. Aeschbach-Hertig and others (2000) proposed a closed-system equilibration (CE) model of fractionated excess air that results from a gas phase (entrapped air-bubble), A_e , that is partially dissolved into a solution due to increased hydrostatic pressure ([eq. 17](#)). The fractionation of the gases dissolved into a solution is governed by the solubilities of the gases, which again tends to fractionate the lighter gases with lower solubilities relative to the heavier gases with higher solubilities ([fig. 1D](#)). Thus, water following this model will be enriched in heavier gases as compared to the lighter gases. For the CE model, the F parameter relates the final and initial gas volumes of the entrapped air, such that $F = \frac{V_b}{V_a}$, where V_a and V_b are the initial and final gas volumes. Commonly, the final volume of the gas phase is smaller than the initial volume such that the F parameter typically ranges from zero (complete dissolution of entrapped air into solution and excess air is unfractionated) to 1 (no excess air formed). A unique feature of this model is that it also can describe degassing or the formation of a gas phase (air bubble) in water. In this case, a drop in the total gas pressure could lead to the formation of a bubble such that the final volume is greater than the initial volume. In this case, the F parameter is greater than 1—see example 5.

10 DGMETA (v.1): Dissolved Gas Modeling and Environmental Tracer Analysis Computer Program

DGMETA uses the following equations for the excess air concentration in water:

UA model:
$$C_a = xA \quad (15)$$

PR model:
$$C_a = xA \exp\left(-F \frac{D}{D_{Ne}}\right) \quad (16)$$

CE model:
$$C_a = \frac{xA_e(1-F)}{1 + \frac{xA_e F}{C_{eq}}} \quad (17)$$

where

- C_a is the dissolved concentration of a gas in excess of air-water equilibrium from the entrainment of air in water in cm³ (STP) per g of water,
- x is the dry-air mole fraction of the gas in the atm in mole fraction,
- A is the amount of air dissolved in water in cm³ (STP) per g of water,
- D is the molecular diffusion coefficient of the gas,
- D_{Ne} is the molecular diffusion coefficient of Ne,
- A_e is the amount of entrapped air as a gas phase in water in cm³ (STP) of air per g of water,
- F is the fractionation parameter that describes the degree of diffusive fractionation when used with the PR model or the final to initial volume of entrapped air (A_e) when used with the CE model, and
- C_{eq} is the solubility concentration in equilibrium with the atmosphere in water in cm³ (STP) per g of water.

Diffusion coefficients (D) for gases are computed from the Arrhenius equation:

$$D = B \exp\left(\frac{E_a}{RT}\right) \quad (18)$$

where

- B is the diffusion coefficient when the temperature goes to infinity, in square meters per second (m²/s),
- E_a is the activation energy in J per mol,
- R is the gas constant (8.3143 J per mol per Kelvin), and
- T is the temperature in Kelvin.

Diffusion coefficients were compiled for He, Ne, Kr, Xe, CO₂, and CH₄ from Jähne and others (1987); for

Ar from Holocher and others (2002); for N₂ and O₂ from Ferrell and Himmelblau (1967); for chlorofluorocarbons-11, -12 from Zheng and others (1998); and SF₆ from King and Saltzman (1995).

Inverse Modeling of Dissolved Gases

DGMETA can compute best-fit parameter estimates for temperature, salinity, elevation (pressure), excess air (or entrapped air), fractionation of gases, and excess N₂ for different models of excess air and solubility equations. Best-fit parameters are determined from inverse methods that solve [equation 1](#) repeatedly until the error between modeled and measured concentrations, relative to the measurement error, is minimized.

DGMETA uses an inverse modeling method similar to that described by Ballentine and Hall (1999) and Aeschbach-Hertig and others (1999). More specifically, DGMETA uses a weighted, nonlinear least-squares parameter-estimation routine that was originally developed from the Gauss-Newton method (with scaling parameter) described by Johnson and Faunt (1992) and modified to allow for constrained parameters. The Jacobian matrix is numerically estimated using the five-point Lagrange differentiation. Standard errors of the fitted parameters are from the diagonal terms of the variance-covariance matrix.

Model fits are computed by minimizing the chi-square test statistic between measured and modeled gas concentrations relative to the gas concentration error:

$$\chi^2 = \sum_{i=1}^n \frac{(O_i - M_i)^2}{\sigma_i^2} \quad (19)$$

where

- n is the number of modeled gases,
- O_i is the observed (measured) concentration of the i -th gas,
- M_i is the modeled total gas concentration ([eq. 1](#)) of the i -th gas, and
- σ_i is the standard error of the observed (measured) concentration of the i -th gas.

The chi-square probability is calculated using the chi-square distribution and the degrees of freedom (number of gases minus the number of model-fit parameters). Chi-square probabilities are only calculated for models having a degree of freedom greater than zero.

Temperature is constrained to the range of 0–100 °C. Excess air/entrapped air is constrained to the range of 0–250 cm³/kg. Salinity is constrained to the range of 0–50 per mil (or g/kg). Pressure is constrained by elevation and can range from –2,000 to 10,000 m above sea level, which corresponds to about 1.2–0.26 atm. Fractionation is constrained to the range of 0–5. Excess N₂ is constrained to the range of 0–500 mg/L as N.

Monte Carlo Simulations

Monte Carlo simulations are included in this program to provide better estimates of the parameter uncertainty for dissolved gas models. For some models, like the CE model, parameter uncertainties can be larger than the computed parameter estimates. This can occur when the F parameter in the CE model approaches the inflection point at 1 (0.8 less than F less than 1.2) or when gas samples appear to have more than one model solution or have large entrapped air values (less than 50 cm³/kg)—see Jung and Aeschbach-Hertig (2018) for a more complete description. In cases where the parameter uncertainty is as large or larger than the parameter estimates, the results of the CE model are ambiguous. These large uncertainties become problematic with computing tracer concentrations because the large uncertainties in model parameters produce large uncertainties in computed tracer concentrations. This situation can be less of an issue with more precise gas measurements that have uncertainties of less than 0.5 percent. Uncertainties of gas measurements determined from existing methods are typically between 1 and 5 percent.

One method to assess the error around the best-fit parameters is to compute Monte Carlo simulations. PANGA (Jung and Aeschbach-Hertig, 2018) provides an interactive Monte Carlo method for exploring the individual cases listed above and potentially refining the model estimates in cases where there are multiple solutions. DGMETA also can be used to generate Monte Carlo simulations and store the results in a worksheet, but DGMETA does not provide automated graphical tools to explore the distribution of simulations for patterns. As an alternative, DGMETA can compute parameter uncertainties more locally around the best-fit parameter estimates computed from the inverse modeling method. Calculations of tracer concentrations from these error estimates have lower tracer uncertainties (see example 4).

Monte Carlo simulations are performed by generating random sets of gas concentrations from a normal distribution using the measured gas and error concentration for a sample and then solving for the best-fit model parameters. This process is repeated many times in order to produce a large population of simulations that can provide estimates of the possible solution space and parameter uncertainty in the model. The number of simulations is typically repeated until the variance of the parameter values asymptotically approach a stable value. The number of Monte Carlo simulations needed to give uncertainty estimates is typically greater than 500, but less than 10,000. By default, DGMETA uses 5,000 simulations. The random gas samples and Monte Carlo simulation results can be output to a separate worksheet if needed.

Random sets of gas samples can be generated by one of two options: (1) by assuming the gases are positively correlated and not independent or (2) by assuming complete

independence. The default used by DGMETA is to compute random gas concentrations using option 1. For this option, gas concentrations are computed using a single random number to generate the entire set of gas concentrations. This will produce sets of gases with concentrations that are higher or lower than the original set of concentrations, but within the error of each gas. Alternatively, completely independent sets of gases can be generated. This approach computes a random number for each gas, such that the set of gases produced from this method are truly random. Unfortunately, that approach can generate parameter errors that are as large as the parameters themselves and hence do not improve the model confidence. In these cases, Jung and Aeschbach-Hertig (2018) recommend a more detailed analysis of the Monte Carlo results using PANGA. Alternatively, it is possible to compute parameter uncertainties that are more local to the best-fit parameters using sets of gas concentrations that increase and decrease in unison (option 1). Parameter estimates and their uncertainties computed using these dependent sets of gases tend to more strongly adhere to the best-fit parameter values based on the original gas data in comparison to results obtained from completely independent sets of gas concentrations. Users can choose either Monte Carlo simulation option.

Environmental Tracer Calculations

Environmental tracers such as CFCs, SF₆, Halon-1301, ³He_{trit}, and ⁴He_{rad} can be used to determine the time elapsed since the water was last in contact with the atmosphere. The measured concentrations of these tracers are not typically meaningful because the concentration used for computing the age of water; like the dry-air mole fraction, the amount of He produced from the decay of tritium in water (³He_{trit}), or from the decay of uranium and thorium in rocks (⁴He_{rad}); are calculated quantities that are dependent on the air-water equilibration conditions when the water was last in contact with the atmosphere. Because these conditions (temperature and excess air contribution) are often unknown, they may be estimated or, more frequently, they are determined by inverse modeling of noble gases or Ar-N₂.

DGMETA can compute atmospheric dry-air mole fractions for transient atmospheric gases and concentrations of ³He_{trit} and ⁴He_{rad} using air-water equilibration conditions determined from inverse modeling of dissolved gases. Computations of air-water equilibration conditions and environmental tracer concentrations using DGMETA provides a consistent treatment of data that may have been analyzed at different laboratories and reported in different units. In addition, the concentrations of tracers and their errors computed by DGMETA can be used in newer versions of TracerLPM (Jurgens and others, 2012) to compute water ages using the same error-weighted inverse modeling technique described in this report.

Transient Atmospheric Gases

Trace atmospheric gases, such as CFCs, SF₆, and Halon-1301, have dry-air mole fractions that have increased in the atmosphere over the last 100 years—though mole fractions for the CFCs have been declining since the 1990s. The dry-air mole fraction is computed by rearranging equation 1 and substituting the total concentration for the measured concentration of the gas and ignoring the in situ production term. Equations for the dry-air mole fraction depend on the model of excess air and are computed using the equations below:

UA model:
$$x = \frac{C_s}{G_{(T,S)}(P_h - e_w) + \frac{A}{V}} \quad (20)$$

PR model:
$$x = \frac{C_s}{G_{(T,S)}(P_h - e_w) + \frac{A \exp(-F \frac{D}{L})}{V}} \quad (21)$$

CE model:
$$x = \frac{C_s}{G_{(T,S)}(P_h - e_w) + \frac{\frac{A_e(1-F)}{1 + \frac{F A_e}{G_{(T,S)}(P_h - e_w)}}}{V}} \quad (22)$$

where

- x is the dry-air mole fraction of the gas in the atmosphere in mole fraction,
- C_s is the sample concentration (measured value) of a gas tracer (CFC, SF₆, or Halon-1301) in mols per kg,
- $G_{(T,S)}$ is the solubility function for the Henry solubility coefficient in mols per kg,
- P_h is the local atmospheric pressure in atm,
- e_w is the water vapor pressure in atm,
- A is the excess air component in cm³ (standard temperature pressure) per g of water,
- V is the molar volume of a gas in mol per cm³,
- F is the fractionation parameter that describes the degree of diffusive fractionation when used with the PR model or the final to initial volume of entrapped air (A_e) when used with the CE model,
- D is the molecular diffusion coefficient of the gas,
- D_{Ne} is the molecular diffusion coefficient of Ne, and
- A_e is the entrapped air volume (volume of trapped air per volume of water) in cm³ (standard temperature pressure) per g of water,

Tritogenic Helium-3 and Helium-4

Tritogenic helium-3 and terrigenous He components are computed from the mass balance of ³He and ⁴He and are described in more detail in Schlosser and others (1989), Solomon (2000), and Solomon and Cook (2000). Air-water equilibrium model results are used to determine the concentration of He in solubility equilibrium with the atmosphere (He_{eq}) and the concentration of He originating from excess air (He_a). The amount of terrigenous helium (He_{terr}) is calculated by subtracting the amount of He_{eq} and He_a from the measured total dissolved helium (He_s) in each sample. Terrigenous helium includes He that accumulates in water from ⁴He_{rad} emitted from radioactive decay of uranium and thorium in aquifer materials and He from the Earth's mantle (He_{man}) that has migrated upwards through faults or is released by weathering of volcanic sediments. Terrigenous helium that is dominated by radiogenic sources in the Earth's crust generally has a low ³He/⁴He ratio (R_{terr}) that is typically less than 5 × 10⁻⁸, whereas He_{terr} that is dominated by mantle He generally has high R_{terr} that is typically greater than 5 × 10⁻⁶.

DGMETA determines He_a from dissolved gas modeling results so the calculation of ${}^3He_{trit}$ (Schlosser and others, 1989) is in the equations below:

$${}^3He_{trit} = He_s R_s - (He_s - He_{terr}) R_a + He_{eq} R_a (1 - \alpha) - He_{terr} R_{terr} \quad (23)$$

where

- ${}^3He_{trit}$ is the helium concentration from the decay of tritium in cm^3 (STP) per g of water,
- He_s is the helium concentration of the sample in cm^3 (STP) per g of water,
- R_s is the ${}^3He/{}^4He$ ratio of the sample corrected for the decay of tritium (half-life is equal to 12.32 years; Lucas and Unterweger, 2000) for the time between the dates of sample collection and analysis,
- He_{terr} is the helium concentration of terrigenous origin in cm^3 (STP) per g of water,
- R_a is the ${}^3He/{}^4He$ ratio of air ($R_a = 1.384 \times 10^{-6}$; Clarke and others, 1976),
- He_{eq} is the helium concentration in equilibrium with the atmosphere in cm^3 (STP) per g of water,
- α is the isotopic fractionation factor of He during air-water solubility equilibrium, and
- R_{terr} is the ${}^3He/{}^4He$ ratio of terrigenous helium.

$$He_{terr} = He_s - He_{eq} - He_a \quad (24)$$

where

- He_{terr} is the helium concentration of terrigenous origin in cm^3 (STP) per g of water,
- He_s is the helium concentration of the sample in cm^3 (STP) per g of water,
- He_{eq} is the helium concentration in equilibrium with the atmosphere in cm^3 (STP) per g of water, and
- He_a is the helium concentration of excess air in cm^3 (STP) per g of water.

$$\alpha = \exp\left[-\left(-0.0299645 + \frac{19.8715}{T} + \frac{-1833.92}{T^2}\right)(1 + 0.000464S)\right] \quad (25)$$

where

- α is the isotopic fractionation factor of He during air-water solubility equilibrium,
- T is the temperature of water in Kelvin, and
- S is salinity in per mil or g/kg.

Samples that have He_s less than He_{eq} usually have experienced gas loss or the gases are fractionated. When He_s is less than He_{eq} , calculations of ${}^3He_{trit}$ using [equation 23](#) will underestimate ${}^3He_{trit}$ concentrations in the sample. In these cases, DGMETA will compute ${}^3He_{trit}$ as the excess of solubility equilibrium, which is usually the largest component of He in samples without He_{terr} :

$${}^3He_{trit} = He_s(R_s - R_{eq}) \quad (26)$$

where

- ${}^3He_{trit}$ is the helium concentration from the decay of tritium in cm^3 (STP) per g of water,
- He_s is the helium concentration of the sample in cm^3 (STP) per g of water,
- R_s is the ${}^3He/{}^4He$ ratio of the sample corrected for the decay of tritium (half-life is equal to 12.32 years; Lucas and Unterweger, 2000) for the time between the dates of sample collection and analysis, and
- R_{eq} is the ${}^3He/{}^4He$ ratio of helium in equilibrium with the atmosphere and is equal to the isotopic fractionation factor times the ${}^3He/{}^4He$ ratio of air (αR_a).

For many calculations of ${}^3\text{He}_{\text{trit}}$, the presence of He_{terr} in samples requires the R_{terr} value to be known or to be determined from an analysis of He isotope systematics. In these situations, the samples where ${}^3\text{H}$ is low or absent (tritium-dead) can be used to identify the source and appropriate R_{terr} value to apply to samples with ${}^3\text{H}$. The R_{terr} can often be identified using a modified Weise plot (Weise and Moser, 1987; Stute and others, 1992) where the ratio of He_{terr} normalized to the excess-air-corrected total He concentration, $\text{He}_{\text{terr}}/(\text{He}_s - \text{He}_a)$, is plotted against the ratio of the excess-air-corrected R_s to the R_a .

Figure 2 shows an example of the modified Weise plot with several lines that illustrate possible evolutionary paths for the accumulation of He in water from different sources of He. Water that enters a water body such as an aquifer, for example, will tend to follow a temporal process that starts on the left near the atmospheric equilibrium ratio of water, R_s/R_a , (0.983) and will generally evolve to the right as the water ages and accumulates He from terrigenic sources. In most groundwater systems, water will gain He_{terr} from the decay of uranium and thorium in sediments causing the R_s to evolve along the lower dashed line showing a radiogenic source of He (dashed

line in fig. 2). In some cases, for example, in basaltic rock aquifers or in areas of seismic activity that allow deep mantle gases to migrate upwards along faults (Craig and others, 1978; Plummer and others, 2000), the He in groundwater may be substantially influenced by a mantle-derived He source (He_{man}) and cause R_s/R_a end-member values greater than 5 (dotted line in fig. 2). In other cases, mantle He may be only a minor component caused by the weathering of small amounts of volcanic sediments in an aquifer (Jurgens and others, 2016), and the groundwater may show a mixed signature of mantle and radiogenic sources of He (dashed-dotted line in fig. 2). Tritogenic helium-3 is another source of He. For water that entered a system after 1950, terrigenic sources of He may not be a substantial component of the total He, so the resulting R_s/R_a will mainly reflect the contribution of ${}^3\text{He}$ from the decay of tritium. Samples that exemplify this process will contain ${}^3\text{H}$ and will plot along the red arrow in the upper left of figure 2. Samples with a mixture of post-1950s water and water older than 1,000 years will tend to have multiple sources of He. Samples that contain measurable levels of ${}^3\text{H}$ and substantial amounts of He_{terr} with a radiogenic source may plot above the dashed line on figure 2.

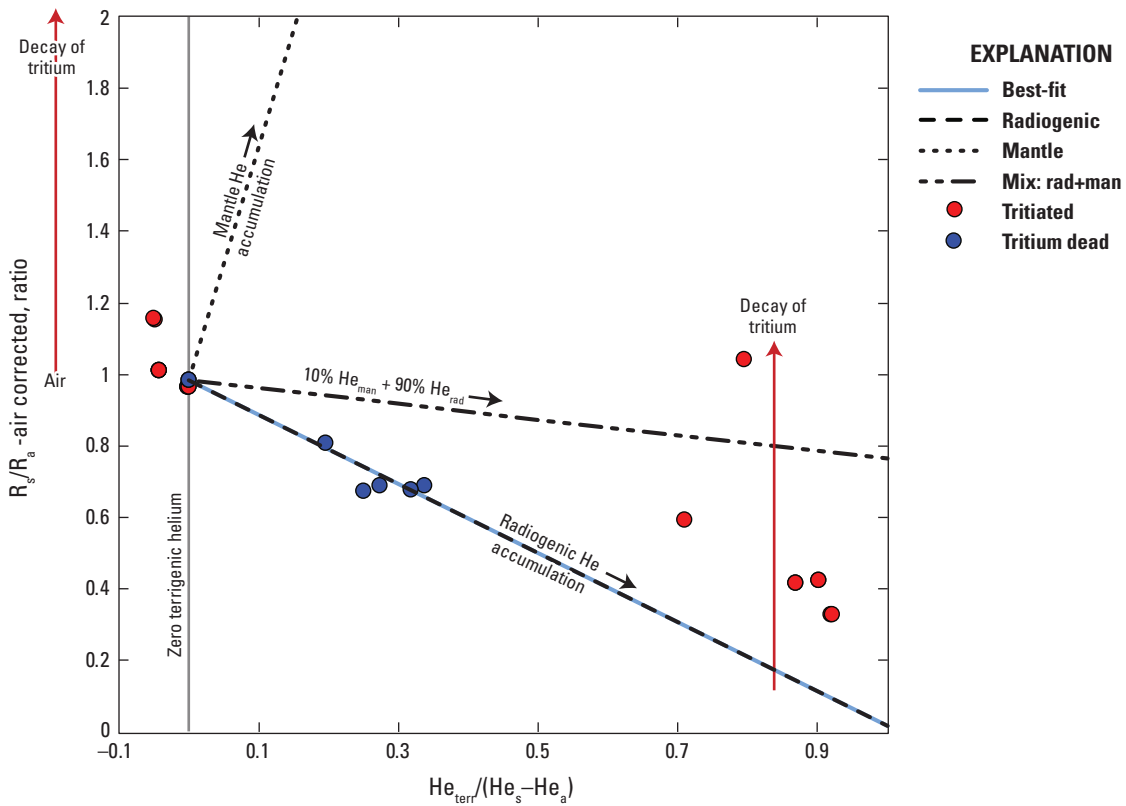


Figure 2. Excess air-corrected helium isotope ratio of the sample relative to air versus the concentration of terrigenic helium as a fraction of the total helium in the sample corrected for excess-air.

To facilitate the He isotope analysis, samples are categorized as either “tritiated” or “tritium dead” using a tritium threshold value that is specified by the user (default is 0.5 tritium unit, TU). DGMETA automatically creates a graph like figure 2 and computes a best-fit line through all tritium-dead samples (blue circles). Those samples are expected to contain the largest proportion of He_{terr} and will usually indicate the R_s/R_a value of the terrigenous source. For the blue samples on figure 2, a radiogenic He source appears to be the main source of He_{terr} and, therefore, the best-fit R_{terr} value is 2 × 10⁻⁸. The best-fit line and R_{terr} value are determined from the equation below:

$$Y = (1 - x)\left(R_{eq} - R_{terr} + \frac{T_b}{He_{eq}}\right) + R_{terr} \quad (27)$$

where

- Y* is the computed *R/R_a* value,
- x* is the excess air corrected value of terrigenous helium (He_{terr}/He_s - He_a),
- R_{eq}* is the ³He/⁴He ratio of helium in equilibrium with the atmosphere and is equal to the isotopic fractionation factor times the ³He/⁴He ratio of air (*αR_a*),
- R_{terr}* is the ³He/⁴He atom ratio of the terrigenous helium,
- T_b* is the background ³He_{trit} in water, and
- He_{eq}* is helium in solubility equilibrium with the atm.

The He isotope graph on the tracer calculation worksheet (“_TrcOut”; fig. 2) is controlled by variables listed in a table to the right of the figure. The table lists the best-fit R_{terr} value computed by the program and this value is used as the default value to calculate ³He_{trit} concentrations using equation 23—see example 4. Changes to the R_{terr} value will affect the graph and ³He_{trit} calculations. The best-fit R_{terr} can be changed manually based on user-defined fits and also can be specified for each sample individually in the ³He/⁴He_{terr} column of the Tracer Output worksheet. Users also can change the percentage of mantle He value and the ³He/⁴He ratio of mantle helium (R_{man}) to explore different mixing lines of radiogenic and mantle He components on the graph (dash-dot-dot line). The default in the DGMETA program is set to 10 percent mantle He.

DGMETA is programmed to only report ³He_{trit} concentrations for samples where the percentage of He_{terr} is less than 70 percent of the total He. Uncertainty in the ³He/⁴He ratio of the He_{terr} can lead to unreliable estimates of ³He_{trit} for

samples with large amounts of He_{terr}. DGMETA computes ³He_{trit} for all samples, but does not report it for samples with He_{terr} greater than 70 percent of the total He; instead, the output includes an additional column with a recommended ³He_{trit} value to report. Tritiogenic helium is not reported for samples with He_{terr} greater than 70 percent of the total He. In cases where the computed ³He_{trit} is small or negative, but the ³H concentration indicates that ³He_{trit} should be present, DGMETA reports a value of less than 1 TU. In other cases, the concentration may not be reliably quantifiable.

Program Description

DGMETA includes an Excel ribbon tab that contains buttons to operate the program and four worksheets for entering sample data or gas solubility data. The DGMETA tab is in the Excel ribbon at the top of the Excel window (fig. 3). The worksheet called SuppInfo contains supporting information on and references to program implementation; models of excess air; equations of local pressure, water density, and vapor pressure; conversion factors; gas solubility formulations used by the program; and a set of sample calculations of pressure, salinity, model gas concentrations, and mole fractions of environmental tracers (fig. 4). The worksheet called Database is used for entering new or modifying existing gas solubility data and properties (fig. 5). The worksheet called Input_Gases is used for entering dissolved gas concentrations (fig. 6), and the worksheet called Input_Tracers is used for entering measurements of environmental tracers (fig. 7). The program is operated from buttons in the DGMETA ribbon menu that can be used to update gas solubility equations, create graphs, model dissolved gases, and calculate tracer concentrations. Some of the subroutines produce worksheets with graphs, model results, or tracer concentrations. Graphs of dissolved gas concentrations are output to a worksheet named by the user with the suffix “_Graphs” appended to the worksheet name. Dissolved gas modeling results are output to a worksheet with the suffix “_ModOut.” Environmental tracer calculations are output to a worksheet with the suffix “_TrcOut.” The “Collapse Tracer Calculation” button will compute average tracer concentrations and results are output to a worksheet with the suffix “_AvgVal.” Flat files with a single-row header can be created for dissolved gas model output files (“_ModOut”), calculated tracer concentrations (“_TrcOut”), or average tracer concentrations (“_AvgVal”).

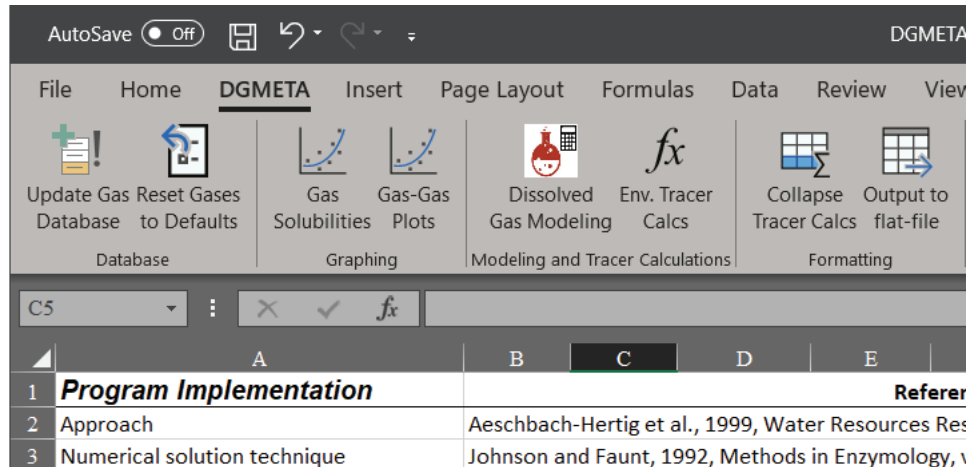


Figure 3. The Dissolved Gas Modeling and Environmental Tracer Analysis tab in the Excel ribbon.

DGMETA Worksheets

The following sections describe the function and purpose of four worksheets included in DGMETA: SuppInfo, Database, Input_Gases, and Input_Tracers. Worksheets colored gray (SuppInfo and Database) are mainly for reference, whereas worksheets colored blue are used for entering sample data.

SuppInfo Worksheet

The SuppInfo worksheet contains supporting information on and references to program implementation; models of excess air; equations of local pressure, water density, and vapor pressure; conversion factors; and gas solubility formulations used by the program (fig. 4). Two important pieces of information are codes used by the program to call up different models of excess air and for specifying the solubility equation of a gas. Worksheet functions are available to calculate total gas concentrations (eq. 1) and mole fractions of gases. These functions use the two-character short name of the excess air model to compute concentrations—see example 3. Examples of how to call up and use the worksheet functions are given at the bottom of the SuppInfo worksheet. When specifying new gas solubility data on the Database worksheet, the solubility equation used by the program is specified by an integer number that refers to one of the equations below the Dissolved Gas Solubility Formulations heading on the SuppInfo worksheet. Note that addition of new gas solubility data and other customizations of DGMETA do not require changes to the SuppInfo worksheet. A calculator for converting between pressure and elevation is provided at the bottom of the worksheet for convenience.

Database Worksheet

The Database worksheet contains a table of solubility coefficients, form of solubility equations, dry-air mole fractions, solubility units, molar volumes, diffusivities, and non-ideal behavior used to calculate the solubility concentration and diffusivity of gases in water. The table can be used for entering new or modifying existing gas solubilities and their formulations (fig. 5). References to source data are provided where applicable. There are comments associated with many fields at the top of the table that contain specific information on the values that can be entered in those fields.

The solubility table is loaded into memory when the program is first opened or when the button “Update Gas Database” is clicked from the DGMETA tab in the Excel ribbon. Users can change the primary solubility equations used for different gases to explore the effects of using different solubility equations on dissolved gas model results—see examples 1 and 2. A value of “Yes” next to the gas (column A) instructs the program to use that formulation for dissolved gas modeling and tracer concentration calculations. The default set of equations are the Weiss solubilities for He, Ne, Ar, and Kr and the Clever solubility for Xe. The program can reset to the default set of gas solubilities using button “Reset Gases to Defaults” from the DGMETA tab in the Excel ribbon (fig. 3).

A unique name for each solubility equation must be specified when entering new gas solubility data on the Database worksheet. Worksheet functions are available to call up gas solubility concentrations for different solubility data. These worksheet functions use the unique name of the gas to call up the solubility formula listed in the solubility table—see example 1.

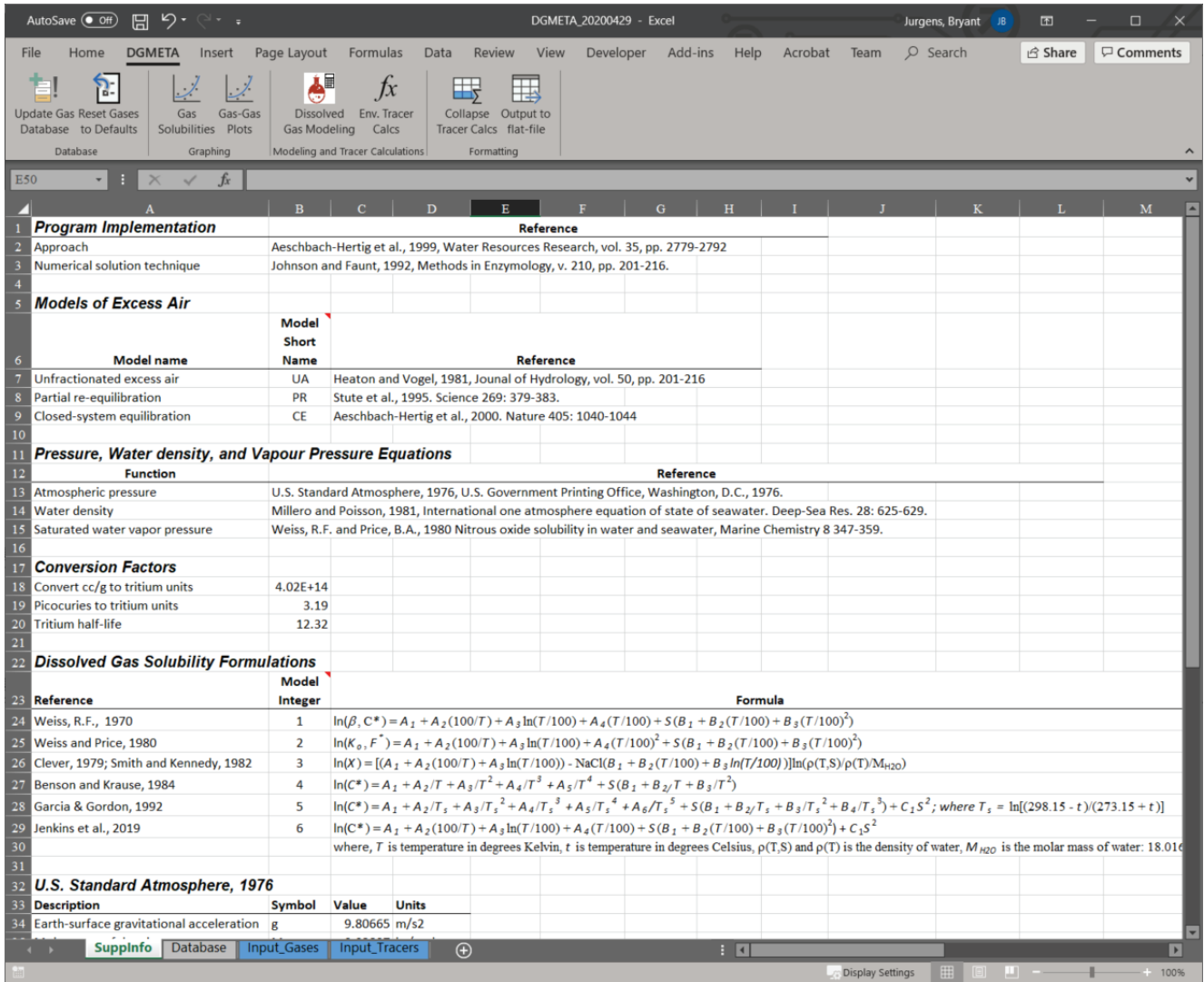


Figure 4. The SupplInfo worksheet, which contains supporting information on and references to program implementation; models of excess air; equations of local pressure, water density, and vapor pressure; conversion factors; gas solubility formulations used by the program; and a set of sample calculations of pressure, salinity, model gas concentrations, and mole fractions of environmental tracers.

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The screenshot shows the 'Database' worksheet in an Excel spreadsheet. The title bar indicates the file is 'DGMETA_20200429 - Excel' and the user is 'Jurgens, Bryant'. The ribbon includes 'DGMETA', 'Insert', 'Page Layout', 'Formulas', 'Data', 'Review', 'View', 'Developer', 'Add-ins', 'Help', 'Acrobat', and 'Team'. The 'DGMETA' ribbon has sub-sections for 'Database', 'Graphing', 'Modeling and Tracer Calculations', and 'Formatting'. The worksheet contains a table with columns for 'Is primary solubility data?', 'Gas Name', 'Gas Short Name', 'Unique name for gas', and five columns labeled 'A1' through 'A5'. The data rows list various gases and their associated numerical values. The bottom of the spreadsheet shows a navigation bar with 'Supplinfo', 'Database', 'Input_Gases', and 'Input_Tracers' tabs, and a status bar at the bottom right showing 'Display Settings' and '100%' zoom.

	A	B	C	D	E	F	G	H	I
1	Gas Solubility and Properties								
2	Is primary solubility data?	Gas Name	Gas Short Name	Unique name for gas	A1	A2	A3	A4	A5
3	Yes	Helium	He	He_Weiss	-167.2178	216.3442	139.2032	-22.6202	--
4	No	Helium	He	He_Clv	-41.4611	42.5962	14.0094	--	--
5	No	Helium	He	He_Jenk	-178.1424181	217.5991006	140.750629	-23.01954354	--
6	Yes	Neon	Ne	Ne_Weiss	-170.6018	225.1946	140.8863	-22.629	--
7	No	Neon	Ne	Ne_WeissB	-39.1971	51.8013	15.7699	--	--
8	No	Neon	Ne	Ne_Clv	-52.8573	61.0494	18.9157	--	--
9	No	Neon	Ne	Ne_H&E	2.18156	1.29108	2.12504	--	--
10	No	Neon	Ne	Ne_Jenk	-274.132929	352.6200943	226.9675886	-37.13393128	--
11	Yes	Argon	Ar	Ar_Weiss	-178.1725	251.8139	145.2337	-22.2046	--
12	No	Argon	Ar	Ar_H&E	2.7915	3.17609	4.13116	4.90379	--
13	No	Argon	Ar	Ar_Clv	-57.6661	74.7627	20.1398	--	--
14	No	Argon	Ar	Ar_Jenk	-227.4606534	305.4346509	180.5278305	-27.99450291	--
15	Yes	Krypton	Kr	Kr_Weiss	-112.684	153.5817	74.469	-10.0189	--
16	No	Krypton	Kr	Kr_Clv	-66.9928	91.0166	24.2207	--	--
17	No	Krypton	Kr	Kr_Jenk	-122.4693886	153.5654326	70.19688875	-8.525241136	--
18	Yes	Xenon	Xe	Xe_Clv	-74.7398	105.21	27.4664	**Salt coef	--
19	No	Xenon	Xe	Xe_Jenk	-224.5100052	292.8234163	157.6126547	-22.66894531	--
20	Yes	Nitrogen	N2	N2_Weiss	-177.0212	254.6078	146.3611	-22.0933	--
21	No	Nitrogen	N2	N2_WeissB	-59.6274	85.7661	24.3696	--	--
22	No	Nitrogen	N2	N2_H&E	6.42931	2.92704	4.32531	4.69149	--
23	No	Oxygen	O2	O2_Weiss	-177.7888	255.5907	146.4813	-22.204	--
24	Yes	Oxygen	O2	O2_B&K	-139.09803	157228.8	-66371490	12436780000	-8.62106E+11
25	No	Oxygen	O2	O2_G&G	5.80818	3.20684	4.1189	4.93845	1.01567
26	Yes	Carbon dioxide	CO2	CO2_Weiss	-162.8301	218.2968	90.9241	-1.47696	--
27	No	Carbon dioxide	CO2	CO2_Weiss_NonIde	-60.2409	93.4517	23.3585	--	--
28	Yes	Methane	CH4	CH4_Wies	-414.3956	599.8626	380.3636	-62.0764	--
29	Yes	Carbon monoxide	CO	CO_Wies	-172.4995	267.6796	161.0862	-25.6218	--
30	Yes	Hydrogen	H2	H2_Wies	-317.1982	459.7398	299.26	-49.3946	--
31	Yes	Nitrous Oxide	N2O	N2O_Weiss	-168.2459	226.0894	93.2817	-1.48693	--
32	No	Nitrous Oxide	N2O	N2O_Weiss_NonIde	-64.8539	100.252	25.2049	--	--
33	Yes	Chlorofluorocarbon-	CFC-11	CFC11_Warner	-136.2685	206.115	57.2805	--	--
34	Yes	Chlorofluorocarbon-	CFC-12	CFC12_Warner	-124.4395	185.4299	51.6383	--	--

Figure 5. The Database worksheet.

Input_Gases Worksheet

The Input_Gases worksheet is used to enter sample information, initial or fixed model values, and dissolved gas concentration data for water samples (fig. 6). Entries for Sample identification (ID), Sample Date, and values for the initial or fixed air-water model parameters are required fields for each sample. Values for the model parameters may be estimated initially and solved for later—see the “Dissolved Gas Modeling” section. Values for salinity and elevation (commonly referred to as the recharge elevation in groundwater studies), and excess air or entrapped air are needed for all models (UA, PR, and CE). The CE and PR models require a value for F. Models that include N₂ as a model constraint require a value for excess N₂, which is most

often set to zero unless there is evidence of denitrification or some other contribution of excess N₂ in the sample. Parameter values are treated as initial starting values when those parameters are optimized during dissolved gas modeling. Parameter values are fixed if the model parameter is not chosen to be optimized. Commonly, salinity and elevation are not optimized so these values are often fixed using site estimates. Salinity can be estimated from measurements of total dissolved solids or from SC using equation 5. The elevation is used to calculate the atmospheric pressure during air-water equilibrium. In groundwater studies, the elevation of air-water equilibrium occurs at the phreatic surface where recharge occurs. The elevation of the well or spring where the dissolved gas sample was collected is often used when the actual recharge elevation is unknown.

Sample Information				Initial or Fixed Air-Water Model Parameters							Select and Enter Gases Below to Model		
Study Unit	Study Area	Sample ID	Sample Date	Record Number / Lab ID	Salinity, per mil or g/kg	Elevation, meters above sea level	Temp, celsius	Excess Air, cm3/kg	Fractionation	Excess N2, mg/L as N	He	errHe	Ne
Mixed	CE model	MER-05	4/3/2006	0060089501	0.2030884	31.0914943	5	3	0.5	0	1.96096E-07	3.92E-09	3.25E-07
Mixed	CE model	MER-12	4/13/2006	0060090701	0.5283579	33.2252243	5	3	0.5	0	1.09897E-07	2.2E-09	2.98E-07
Mixed	CE model	MER-20	5/1/2006	0060098301	0.2584166	98.7612173	5	3	0.5	0	4.47E-09	3.7E-07	1.07E-06
Mixed	CE model	MERFP-01	4/13/2006	0060091001	0.5648326	32.7070328	5	3	0.5	0	1.96096E-07	3.92E-09	3.25E-07
Mixed	CE model	MERMW-05	4/5/2006	0060090501	0.2634484	57.068133	5	3	0.5	0	5.69948E-08	1.14E-09	2.45E-07
Mixed	CE model	MOD-06	3/21/2006	0060076001	0.328332	27.8604175	5	3	0.5	0	3.2392E-07	6.48E-09	2.5E-07
Mixed	CE model	MOD-10	5/3/2006	0060099001	0.1712508	58.6501414	5	3	0.5	0	1.09897E-07	2.2E-09	2.98E-07
Mixed	CE model	TRLK-02	3/16/2006	0060070101	0.150033	32.6155872	5	3	0.5	0	2.34586E-07	4.69E-09	2.17E-07
Mixed	CE model	TRLK-10	3/27/2006	0060079401	0.7559015	14.4514485	5	3	0.5	0	1.06721E-07	2.13E-09	2.4E-07
Mixed	CE model	TRLK-15	4/4/2006	0060089901	0.3037146	31.0914943	5	3	0.5	0	5.88945E-06	1.18E-07	3.58E-07
Mixed	CE model	TRLKMW-01	3/15/2006	0060070601	0.422958	17.9842957	5	3	0.5	0	4.69039E-07	9.38E-09	2.56E-07
Modern	CE model	CE-QPC-01	3/20/2006	0060079001	0.1483581	69.3492733	5	3	0.5	0	6.07369E-08	1.21E-09	2.65E-07
Modern	CE model	MER-02	3/29/2006	0060079701	0.163433	42.6746001	5	3	0.5	0	2.79147E-07	5.58E-09	2.31E-07
Modern	CE model	MER-04	3/30/2006	0060080001	0.2399695	25.60476	5	3	0.5	0	5.36605E-08	1.07E-09	2.23E-07
Modern	CE model	MER-09	4/10/2006	0060092101	0.2153802	55.6111003	5	3	0.5	0	9.49373E-08	1.9E-09	2.67E-07
Modern	CE model	MER-11	4/12/2006	0060090901	0.1589661	78.338373	5	3	0.5	0	1.44582E-07	2.89E-09	3.28E-07
Modern	CE model	MER-16	4/18/2006	0060094301	0.1405427	49.3806087	5	3	0.5	0	6.09794E-07	1.22E-08	2.32E-07
Modern	CE model	MER-17	4/18/2006	0060095701	0.3887897	48.9233808	5	3	0.5	0	6.69725E-08	1.34E-09	2.77E-07
Modern	CE model	MER-19	4/20/2006	0060096101	0.3658326	44.5035115	5	3	0.5	0	6.00788E-08	1.2E-09	2.27E-07
Modern	CE model	MERMW-02	3/27/2006	0060083801	0.288053	47.2468787	5	3	0.5	0	5.35435E-08	1.07E-09	2.36E-07
Modern	CE model	MERMW-03	3/28/2006	0060086701	0.312106	45.1131487	5	3	0.75	0	5.26798E-08	1.05E-09	2.25E-07
Modern	CE model	MERMW-04	3/28/2006	0060083901	0.2215268	45.1131487	5	3	0.5	0	7.15657E-08	1.43E-09	2.33E-07
Modern	CE model	MOD-01	3/13/2006	0060069801	0.2450001	22.0658164	5	3	0.5	0	2.46117E-07	4.92E-09	2.28E-07
Modern	CE model	MOD-02	3/14/2006	0060069901	0.328332	27.8573693	5	3	0.5	0	1.39729E-07	2.79E-09	2.33E-07
Modern	CE model	MODFP-02	3/13/2006	0060070401	0.6378332	19.5083886	5	3	0.5	0	1.25861E-06	2.52E-08	2.22E-07
Modern	CE model	MODMW-01	3/30/2006	0060085301	0.2902902	40.2360515	5	3	0.5	0	5.65916E-08	1.13E-09	2.51E-07
Modern	CE model	TRLK-07	3/23/2006	0060077901	0.0641047	69.3035505	5	3	0.5	0	5.35612E-08	1.07E-09	2.38E-07
Modern	CE model	TRLK-08	3/23/2006	0060077801	0.0769321	57.001073	5	3	0.5	0	6.20147E-08	1.24E-09	2.59E-07
Modern	CE model	TRLK-09	3/23/2006	0060078001	0.0914351	79.8624659	5	3	0.5	0	5.75063E-08	1.15E-09	2.43E-07
Modern	CE model	TRLK-12	4/3/2006	0060090001	0.4263196	20.6057355	5	3	0.5	0	6.03883E-08	1.21E-09	2.3E-07
Modern	CE model	TRLKMW-02	3/15/2006	0060070701	0.4274402	17.9842957	5	3	0.5	0	5.6815E-08	1.14E-09	2.42E-07
Modern	CE model	TRLKMW-03	3/16/2006	0060070801	0.3495988	39.9312329	5	3	0.5	0	6.12179E-08	1.22E-09	2.69E-07
Modern	CE model	TRLKMW-04	3/16/2006	0060070901	0.3171413	39.9312329	5	3	0.5	0	5.7448E-08	1.15E-09	2.65E-07
Modern	CE model	TRLKMW-05	3/29/2006	0060085901	0.6659285	39.6264144	5	3	0.5	0	5.37215E-08	1.07E-09	2.26E-07

Figure 6. The Input_Gases worksheet and the Dissolved Gas Modeling and Environmental Tracer Analysis tab in the Excel ribbon.

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Dissolved gas concentrations and uncertainty for each sample are entered below the section “Select and Enter Gases Below to Model Air-Water Equilibrium Conditions or Graph.” Each gas requires an estimate of the measurement uncertainty (usually 1 standard error) in order to find the best-fit solution to the data. Measurement uncertainty for dissolved gases can vary by gas and analytical method, but are typically between 1 and 5 percent of the measured value.

The list of gases in columns below the section “Select and Enter Gases Below to Model Air-Water Equilibrium Conditions or Graph” can be changed to different gases and different concentration units by the user. Worksheet cells that have blue text contain a drop-down list of gases or units (fig. 6). Row 2 contains a list of gases and row 3 contains a list of units that the program will accept. The list of gases in the drop-down menu is controlled by the list of gases entered

on the Database worksheet. Adding new gases to the Database worksheet will expand the gases listed in the drop-down menus on the Input_Gases worksheet.

Input_Tracers Worksheet

The Input_Tracers worksheet is used to enter laboratory results for ^3H , He isotopes, dissolved gas data, and transient atmospheric gas tracers (fig. 7). The program uses the tracer information on this worksheet to calculate environmental tracer concentrations of dry-air mole fractions and He components from dissolved gas model results listed in a dissolved gas modeling output worksheet, which is identified by the suffix “_ModOut.” Dissolved gas model output is based on information entered on the Input_Gases worksheet so samples entered on the Input_Tracers worksheet should correspond to samples entered on the Input_Gases worksheet.

Sample Information					Tritium-Helium analysis									
Study Unit	Study Area	Sample ID	Sample Date	Record Number / Lab ID	^3H	err_3H	$\delta^3\text{He}$	$\text{err}_\delta^3\text{He}$	$^3\text{He}/^4\text{He}$ atom ratio	$\text{err}_3\text{He}/^4\text{He}$ atom ratio	He	errHe	Neon	errN
					pCi/L	pCi/L	%	%			cm3/g		cm3/g	
Merced	Mixed	MER-01	3/27/2006	0060079501	2.3925	0.2871			3.04E-07	2.28E-09	4.3E-06	8.61E-08	2.3E-07	4.66
Merced	Mixed	MER-03	3/30/2006	0060079801	5.0721	0.5742			6.16E-07	4.62E-09	1.1E-06	2.19E-08	2.21E-07	4.42E
Merced	Mixed	MER-05	4/3/2006	0060089501	1.7545	0.1914			6.14E-07	4.61E-09	4.86E-07	9.71E-09	2.19E-07	4.38E
Merced	Mixed	MER-07	4/6/2006	0060089701	5.2635	1.1803			1.45E-06	1.09E-08	9.44E-08	1.89E-09	2.41E-07	4.82E
Merced	Mixed	MER-08	4/6/2006	0060090601	6.2524	0.2871								
Merced	Mixed	MER-12	4/13/2006	0060090701	5.0721	0.9889			1.02E-06	7.62E-09	1.73E-07	3.47E-09	3.7E-07	7.41E
Merced	Mixed	MER-14	4/17/2006	0060095501	3.0624	0.4147			5.7E-07	4.27E-09	2.48E-06	4.96E-08	2.2E-07	4.4E
Merced	Mixed	MER-18	4/19/2006	0060095901	1.6269	0.2871			1.07E-06	8.05E-09	8.56E-08	1.71E-09	2.77E-07	5.54E
Merced	Mixed	MER-20	5/1/2006	0060098301	1.595	0.9889			4.68E-07	3.51E-09	1.33E-06	2.65E-08	1.07E-06	2.14E
Merced	Mixed	MER-22	5/2/2006	0060098701	1.7545	0.2871			3.07E-07	2.31E-09	2.31E-06	4.62E-08	2.16E-07	4.33E
Merced	Mixed	MER-23	6/11/2006	0060122001	1.7864	0.1914			7.34E-07	5.51E-09	1.53E-07	3.06E-09	2.23E-07	4.46E
Merced	Mixed	MERFP-01	4/13/2006	0060091001	2.871	0.9889			8.94E-07	6.71E-09	1.96E-07	3.92E-09	3.25E-07	6.51E
Merced	Mixed	MERMW-05	4/5/2006	0060090501	6.699	0.9889			1.39E-06	1.04E-08	5.7E-08	1.14E-09	2.45E-07	4.91E
Merced	Modern	MER-02	3/29/2006	0060079701	16.588	1.276			1.13E-06	8.47E-09	2.79E-07	5.58E-09	2.31E-07	4.63E
Merced	Modern	MER-04	3/30/2006	0060080001	11.6435	0.6061			1.51E-06	1.13E-08	5.37E-08	1.07E-09	2.23E-07	4.45E
Merced	Modern	MER-09	4/10/2006	0060092101	16.588	1.276			1.83E-06	1.37E-08	9.49E-08	1.9E-09	2.67E-07	5.33E
Merced	Modern	MER-10	4/11/2006	0060092201	14.993	1.276			1.84E-06	1.38E-08	1E-07	2E-09	2.43E-07	4.86E
Merced	Modern	MER-11	4/12/2006	0060090901	15.3758	0.9889			1.45E-06	1.09E-08	1.45E-07	2.89E-09	3.28E-07	6.57E
Merced	Modern	MER-15	4/18/2006	0060095601	26.9874	1.0846			2.65E-06	1.99E-08	5.06E-08	1.01E-09	2.14E-07	4.29E
Merced	Modern	MER-16	4/18/2006	0060094301	14.8654	0.6699			8.88E-07	6.66E-09	6.1E-07	1.22E-08	2.32E-07	4.64E
Merced	Modern	MER-17	4/18/2006	0060095701	15.9819	0.8294			1.4E-06	1.05E-08	6.7E-08	1.34E-09	2.77E-07	5.55E
Merced	Modern	MER-19	4/20/2006	0060096101	36.4936	1.4993			1.96E-06	1.47E-08	6.01E-08	1.2E-09	2.27E-07	4.55E
Merced	Modern	MERMW-01	3/27/2006	0060085001	14.993	1.276			1.58E-06	1.19E-08	4.07E-08	8.15E-10	1.83E-07	3.65E
Merced	Modern	MERMW-02	3/27/2006	0060083801	25.5838	1.595			3.41E-06	2.56E-08	5.35E-08	1.07E-09	2.36E-07	4.71E
Merced	Modern	MERMW-03	3/28/2006	0060086701	30.9749	1.8821			4.77E-06	3.58E-08	5.27E-08	1.05E-09	2.25E-07	4.49E
Merced	Modern	MERMW-04	3/28/2006	0060083901	13.7808	1.276			2.02E-06	1.51E-08	7.16E-08	1.43E-09	2.33E-07	4.66E
Merced	PreModern	MER-06	4/6/2006	0060087101					6.4E-07	4.8E-09	1.77E-06	3.53E-08	2.24E-07	4.48E
Merced	PreModern	MER-13	4/13/2006	0060090801	1.0846	0.6061			1.23E-06	9.21E-09	1.08E-07	2.15E-09	3.19E-07	6.38E
Merced	PreModern	MER-21	4/5/2006	0060087601	0.2871	0.5742			1.01E-06	7.61E-09	7.05E-08	1.41E-09	2.08E-07	4.16E
Merced	PreModern	MERFP-02	5/1/2006	0060098401	0.49445	0.9889			8.58E-07	6.43E-09	7.96E-08	1.59E-09	2.08E-07	4.15E
Modesto	Mixed	MOD-04	3/20/2006	0060075901	4.9445	0.2871			1.59E-06	1.2E-08	7.08E-08	1.42E-09	2.34E-07	4.68E
Modesto	Mixed	MOD-06	3/21/2006	0060076001	7.656	0.4147			9.61E-07	7.21E-09	3.24E-07	6.48E-09	2.5E-07	5E
Modesto	Mixed	MOD-09	3/23/2006	0060078101	3.19	0.9889			1.67E-06	1.25E-08	5.74E-08	1.15E-09	2.6E-07	5.19E
Modesto	Mixed	MOD-10	5/3/2006	0060099001	4.8169	0.3828			1.91E-06	1.43E-08	1.1E-07	2.2E-09	2.98E-07	5.95E

Figure 7. The Input_Tracers worksheet and the DGMETA (Dissolved Gas Modeling and Environmental Tracer Analysis) tab in the Excel ribbon.

The first several columns of the Input_Tracers worksheet pertain to sample information. The Sample ID and Sample Date are used to pair environmental tracer measurements on the Input_Tracers worksheet with samples listed in a dissolved gas modeling output worksheet. As such, multiple dissolved gas models and multiple rows of tracer measurements will produce multiple rows of calculated environmental tracer concentrations on the Environmental Tracer Output worksheet (“_TrcOut”).

Measurements of ^3H , isotopes of He ($^3\text{He}/^4\text{He}$), He, and Ne are used to compute the concentration of He derived from the decay of tritium ($^3\text{He}_{\text{trit}}$) and the amount of He_{terr} in a sample. Measured concentrations of these constituents are entered below the column “Tritium-Helium analysis.” Helium isotope concentrations and errors can be entered as $\delta^3\text{He}$ or R_s . If the analysis date of the He isotope measurement is provided by the user, the isotopes will be corrected for the decay of tritium between the sample date and the analysis date. If the analysis date is unknown, the program will use a presumed analysis date that is 6 months after the sample date. The measurement uncertainty must also be entered or estimated for each measured value.

Atmospheric Gas Tracers are listed to the right of Tritium-Helium analysis (not shown in [fig. 7](#)). For each gas listed in the “Atmospheric Gas Tracers” section, the program will compute the dry-air mole fraction in the Environmental Tracer Output worksheet (_TrcOut). The list of gases can be modified by the user for cells with blue text. Worksheet cells that have blue text contain a drop-down list of gases or units. Row 2 contains a list of gases and row 3 contains a list of units that the program will accept. The list of gases in the drop-down menu is controlled by the list of gases entered in the Database worksheet. Adding new gases to the Database worksheet will expand the gases listed in the drop-down menus on the Input_Gases and Input_Tracers worksheets.

DGMETA Operation

The DGMETA tab is used to operate the program ([fig. 3](#)). The buttons on the tab are organized into four areas of program functionality: Database, Graphing, Modeling and Tracer Calculations, and Formatting.

Database

There are two buttons that cause the database, stored in memory, to change. The first button called “Update Gas

Database” is used when changes to the database table are made. Additional gases can be added to the database by following the formatting and conventions provided on the Database worksheet. The field comments at the top of the database table can contain specific information on the values that can be entered in those fields. The button “Update Gas Database” also will need to be clicked when changes to the existing gases are made. For example, many reactive gases, like CO_2 , have transient atmospheric mole fractions (mixing ratios) not just the environmental trace gases. As such, it may be necessary to adjust the mole fractions of these gases for calculating solubility and modeling biogeochemical reactions. In addition, the reactive gases can be included as tracers and their mole fractions can be derived from dissolved gas modeling results.

A common use of the Update Gas Database function is to test the fit of various solubility data to sample gas concentrations during dissolved gas modeling. Dissolved gas modeling fits are performed with the set of solubility data indicated with a “Yes” next to the gas name. To change the default set of solubility data, replace the “Yes” with a “No” for updated solubility data and replace the “No” with a “Yes” for the desired solubility data. For each gas, only one set of solubility data can be chosen as the primary solubility data. Example 2 tests the fit of different sets of solubility data to air-equilibrated and seawater samples. The second button, “Reset Gases to Defaults,” will reset the primary solubility data values to the defaults. The set defaults are the Weiss solubilities for He, Ne, Ar, and Kr and the Clever solubility (with salting coefficients from Smith and Kennedy, 1983) for Xe. These solubilities are the most commonly used for groundwater studies of past recharge temperatures and age dating (Aeschbach-Hertig and others, 1999; Kipfer and others, 2002; Aeschbach-Hertig and Solomon, 2013).

Graphing

Graphs are a simple way to aid the evaluation of dissolved gas models to fit sample data and to evaluate the behavior of gases under different conditions. DGMETA can create two types of interactive graphs: (1) graphs of the solubility of gases in water at equilibrium with the atm and (2) graphs of gas concentrations of samples with dissolved gas model output. Users are encouraged to explore the Graphs worksheet to see how built-in functions can be used to create custom graphs and functionality.

Gas Solubilities

The solubility of a gas in water can be graphed using the “Gas Solubilities” button on the DGMETA tab (fig. 3). This button will display a form (fig. 8) that can be used to select gases and graph their solubility in water over a range of temperature, elevation (pressure), and salinity conditions (fig. 8). The list of gases displays the unique name entered in the database table. The user can specify which conditions to vary (temperature, elevation, or salinity values), the range of parameter values, the step increment, the values of fixed parameters (temperature, elevation, or salinity), and the units of the concentrations. Example 1 uses this routine to examine the solubility of Ne in water and seawater for different sets of Ne solubility data. Once the form is complete, the “CREATE

Figure 8. The form used for creating graphs of the solubility of a gas in water at equilibrium with the atmosphere.

GRAPH” button will create a new worksheet with a name specified by the user and a suffix of “_SolGph,” and this new worksheet will contain a graph of the solubility concentration in water (fig. 9).

_SolGph Worksheet

The _SolGph worksheet is organized into three sections: (1) the graphical display of charts, (2) a set of control variables that can be adjusted to change the graph, and (3) a section below the control variables that contains formulas for calculating the dissolved gas concentration (fig. 9). The worksheet has a set of control variables that are initially populated by the program based on the values specified on the form by the user (fig. 8). The values on the worksheet can be changed to see how the solubility of a gas is affected.

Gas-Gas Graphs

Graphs of gas concentrations from samples and from model output can be created to evaluate different models of dissolved gas concentrations (UA and CE) that might explain measured concentrations in samples. The “Gas-Gas Plots” button will display a form named “Create Graphs” that can be used to select samples to graph from the Input_Gases worksheet or from the Output of Dissolved Gas Models (_ModOut) worksheet (fig. 10)—see the “Dissolved Gas Modeling” section. Up to four graphs can be created, and graphs can include selected ratios of gases in addition to the gas concentrations. Samples can be plotted as groups according to their labels entered in the Study Area column on the Input_Gases or _ModOut worksheets; although these worksheets should be sorted by Study Area before plotting the samples as groups.

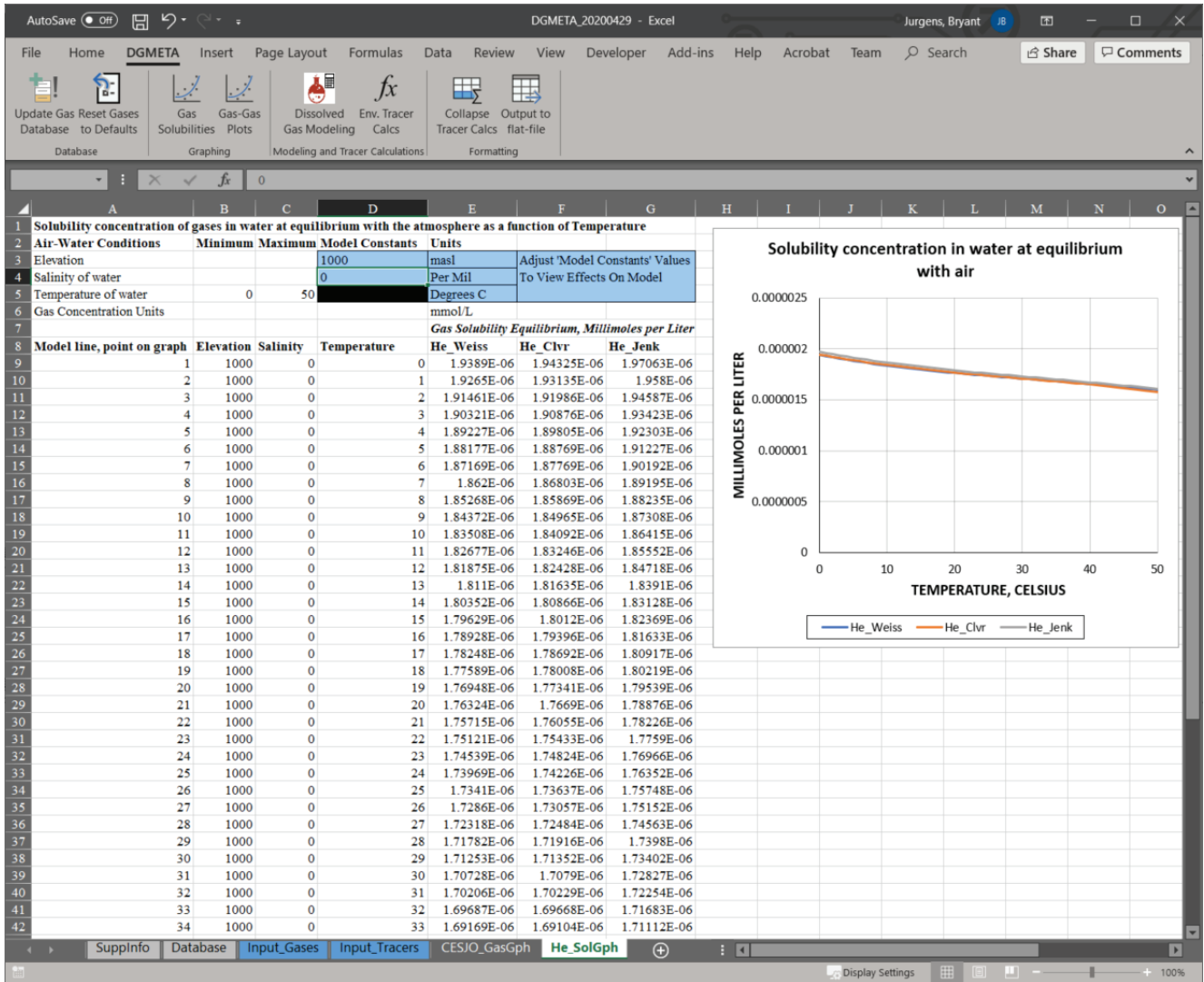


Figure 9. The _SolGph worksheet created by the program that is used to compute and graph the solubility of a gas in water with different temperature, elevation (pressure), and salinity conditions.

1. Select worksheet with gas samples

Input_Gases

2. Select samples to graph

Graph all samples

Select the number of graphs

1 2 3 4

Plot study areas as separate series on graphs

Sample ID	Row Num
301420095093201	4
301420095093201	5
300413094402101	6
300413094402101	7
304603094101801	8
304603094101801	9
300932094005301	10
300932094005301	11
292923095091601	12
292923095091601	13
291949095024801	14
291949095024801	15
305947093395001	16
305947093395001	17
302145095473901	18
302145095473901	19
303000095002001	20
303000095002001	21
292944095550101	22
292944095550101	23
272638098532301	24
272638098532301	25

Graph 1

X-axis: Ar/Ne

Y-axis: N2

Graph 2

X-axis: Ar

Y-axis: N2

CREATE GRAPHS CANCEL

Figure 10. The form used for creating graphs of gas concentrations from samples and dissolved gas models.

_GasGph Worksheet

The Create Graphs program will create a new worksheet with a suffix of “_GasGph” that contains interactive graphs with a set of control variables above each graph, which are used for exploring sample gas concentrations in relation to modeled dissolved gas concentrations from the UA and CE models (fig. 11). Each graph created on a _GasGph worksheet will have a set of black lines that correspond to a range in temperatures (0–40 °C) and amounts of UA (0–10 cm³/kg). The black lines will generally bound most well-behaved samples. Samples that plot outside the black lines can indicate degassed samples (see example 5), extreme F of gases, and samples that have undergone in situ production of gases, such as radiogenic helium or denitrification (see examples 3 and 4).

Each graph also will include a green line of the UA model that spans across the bounded range of black lines and a red-dotted line of fractionated excess air (CE model) for various amounts of entrapped air (0–200 cm³/kg; fig. 11). The position of the UA model (green line) and CE model will move based on changes to the temperature value set in the control variables above each graph. The CE model also will change shape based on changes to the F value. Graphs that include N₂ gas concentrations will have an orange line that shows UA for various amounts of excess N₂ gas (0–10 mg/L as N) that could be contributed by denitrification or deep fluids. The origin of the excess N₂ gas line will intersect the UA model line by the value set in the “Init. excess air (UA), cm³/kg” field.

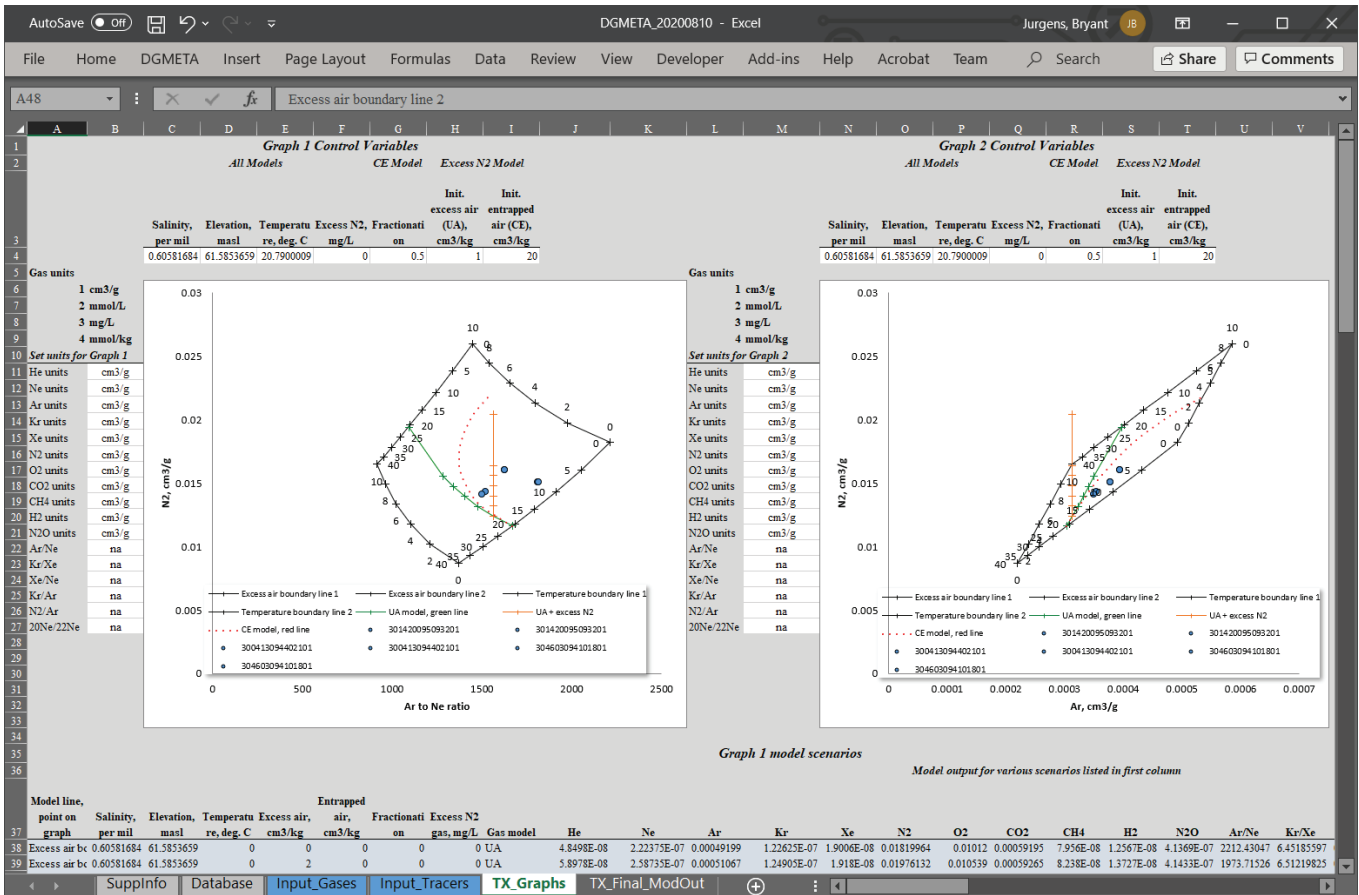


Figure 11. An example `_GasGph` worksheet created by the program to compute and graph gas concentrations for samples and models.

Above each graph is a set of variables that control the lines on each graph (fig. 11). The values are initially set by the program based on averages of the initial values on the `Input_Gases` worksheet or best-fit values from a `_ModOut` worksheet. The values for salinity and elevation affect the gas concentrations for all lines displayed. The value for temperature affects the lines for the UA model (green line), CE model (red-dotted line), and excess N₂ (orange line). The “Init. excess air (UA), cm³/kg” field affects the position of the excess N₂ line and the F value affects the CE model.

To the left of each graph is a set of controls for setting the units of gas concentrations (fig. 11). These can be changed to display gases in units of (1) cm³/g, (2) mmol/L, (3) mg/L, or (4) mmol/kg. Gas concentrations are converted to different units using equations 10–11.

The `_GasGph` worksheets also contain calculations for the different gas models and the sample concentrations converted to different units. These calculations call up custom Excel worksheet functions that can be manipulated and used to create custom calculations and graphs to suit user needs.

Dissolved Gas Modeling

DGMETA is used most often to compute dissolved gas models and environmental tracer concentrations; these tasks are completed in three steps: (1) enter dissolved gas measurements on the `Input_Gases` worksheet and environmental tracer measurements on the `Input_Tracers` worksheet, (2) compute dissolved gas models for samples listed on the `Input_Gases` worksheet, and (3) compute environmental tracer concentrations for samples listed on the `Input_Tracers` worksheet using the dissolved gas models computed from step 2. Dissolved gas models can be computed using the “Dissolved Gas Modeling” button in the DGMETA tab (fig. 3). This program will compute best-fit estimates of temperature, excess air, and other model parameters and will report the results in a program created output worksheet with the suffix “`_ModOut`.” Environmental tracer concentrations can be computed using the “Env. Tracer Calcs” button in the DGMETA tab. For samples listed in the `_ModOut` worksheet, environmental tracer concentrations will be computed for every corresponding Sample ID and Date listed on the `Input_Tracers` worksheet. Tracer calculations will be reported on a worksheet created by the program with the suffix “`_TrcOut`.”

The program for modeling dissolved gases is initiated from the “Dissolved Gas Modeling” button in the DGMETA tab in the Excel ribbon (fig. 3). This button will display the Dissolved Gas Modeling form, which allows users to select one or more samples to model, gases to include in the model, parameters to optimize, and one or more models to evaluate (fig. 12). The user also has several model options that can be included. The first option enables the program to automatically rerun models with poor fits by removing the gas with the poorest fit in an attempt to look for an acceptable model solution for the sample. The program defines a poor fit as a model with a chi-square probability less than 1 percent or 0.01—see example 4. The second option enables the program to calculate excess N_2 for samples where dissolved N was measured, but is not included as a model-fit parameter such that the dissolved gas model is based on measured gases other than N. For example, if noble gases and N were measured in a sample, a user could select Ne, Ar, Kr, and Xe for modeling the temperature and excess air, and the program would subsequently calculate the amount of excess N_2 using the model results and the dissolved N measurement. Alternatively, the user could include excess N_2 as a model-fit parameter. The third option will run Monte Carlo simulations for models with acceptable probabilities in order to more accurately define the parameter errors. The user can choose the number of simulations and to output all the simulation results in a separate worksheet. The fourth option, Excess N_2 for Ar/ N_2 only, allows users to solve for excess N_2 gas for a range of excess air values (see example 3) when only Ar and N_2 were measured. This analysis computes a set of dissolved gas

models by setting excess air to a constant value incrementally over a range of values and computing the best-fit recharge temperature and excess N_2 value. If the N_2 values are greater than or equal to zero, the model is accepted and the average and standard deviation of the set of accepted models are returned as the best-fit parameter and parameter error values.

_ModOut Worksheet

Results of dissolved gas modeling are output to a worksheet named by the user with the suffix “_ModOut” appended to the name (fig. 13). All sample information, initial model parameter values, dissolved gas modeling results, measured concentrations, modeled concentrations, and Monte Carlo results are written to the output worksheet. Results of dissolved gas modeling include the model-fit and optimal parameters and their uncertainty. If a parameter was not included in the best-fit parameter, but was required by the model, then the initial value was used (“init. val.”). Only the CE and PR models require a value for F, and only samples with dissolved N can be used to estimate excess N_2 ; all other parameters are required. The gas with the highest contribution to the chi-square error, deviations between measured and modeled solubility concentrations, and generic comments about the gas concentrations and model results are provided to help evaluate the model results. Modeled gas solubility, excess air, and total gas concentrations are provided in cm^3 at STP per g of water, mmol/L, and mg/L. If the CE model was used to find the best-fit parameter of entrapped air, then the equivalent excess air concentration for each gas is calculated and included in the output.

Dissolved Gas Modeling

1. Select samples to model

2. Select gases to model

3. Select parameters to model

4. Select models and options

Model all samples

Sample ID	Row Num
MER-05	4
MER-12	5
MER-20	6
MERFP-01	7
MERMW-05	8
MOD-06	9
MOD-10	10
TRLK-02	11
TRLK-10	12
TRLK-15	13
TRLKMW-01	14
CE-QPC-01	15
MER-02	16
MER-04	17
MER-09	18
MER-11	19
MER-16	20
MER-17	21
MER-19	22
MERMW-02	23
MERMW-03	24
MERMW-04	25

He, cm³/g
Ne, cm³/g
Ar, cm³/g
Kr, cm³/g
Xe, cm³/g
N₂, cm³/g
Ar, mg/L
N₂, mg/L
O₂, mg/L
CO₂, mg/L
CH₄, mg/L
H₂, mg/L
N₂O, mg/L

Parameters

Temperature

Excess air

Salinity

Elevation / pressure

Fractionation (excess air)

Excess nitrogen gas

Models

Unfractionated excess air (UA)

Partial re-equilibration (PR)

Closed-system equilibration (CE)

Model options

Use alt. search method

Rerun bad fits with reduced gases

Calculate excess nitrogen gas

Run Monte Carlo simulations

Excess N₂ for Ar/N₂ only

5. RUN MODELS

CLOSE FORM

Figure 12. The form for modeling dissolved gases.

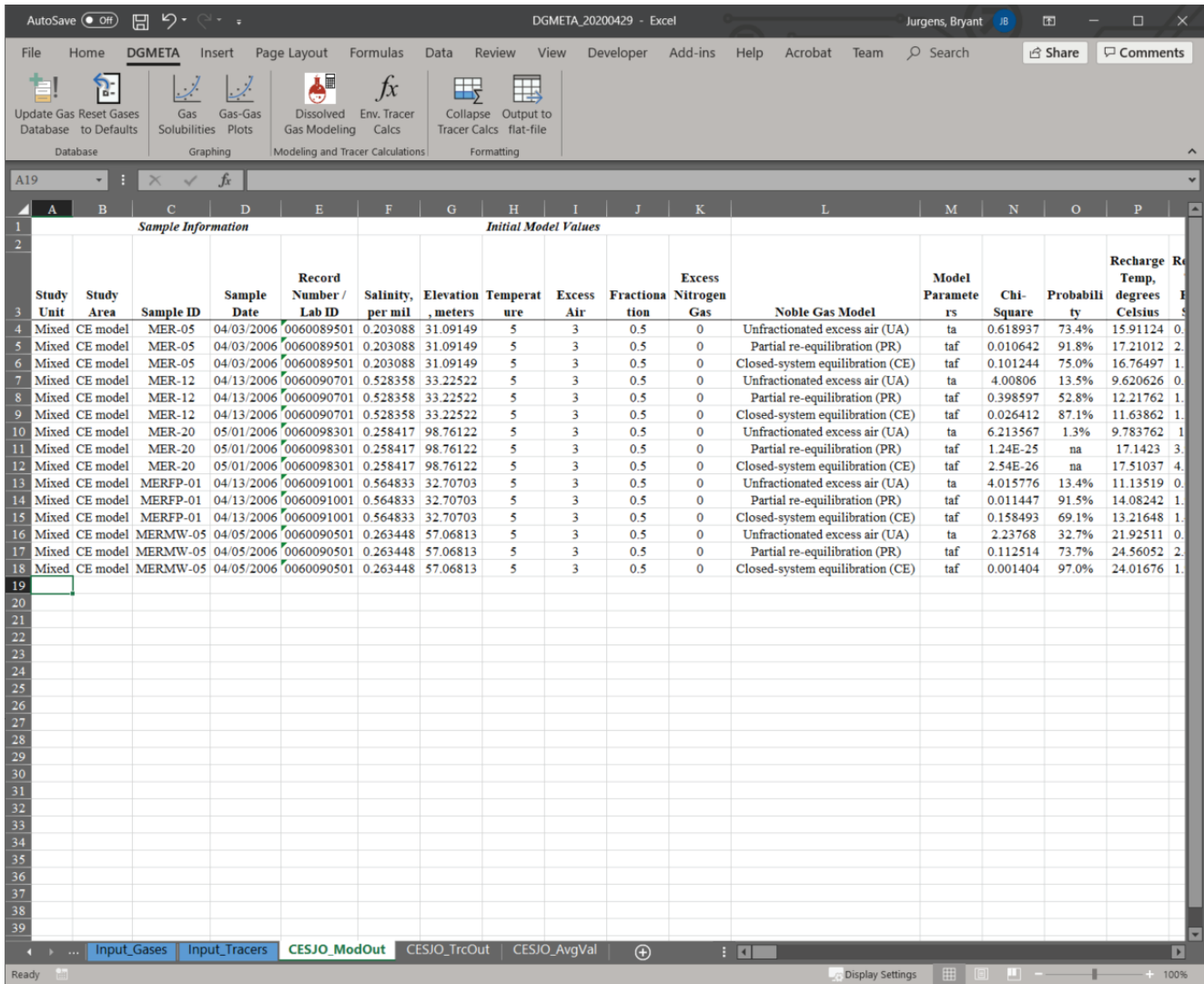


Figure 13. The `_ModOut` worksheet. There are more than 250 columns of values that are produced in the output, organized into groups that relate fields to sample information, initial model values, model results, measured concentrations and computations of model components and Monte Carlo results.

Monte Carlo simulation results are provided in the last set of columns in the worksheet and contain the results of the average and standard deviations of modeled simulations. When computing tracer concentrations from dissolved gas model results where Monte Carlo simulations were computed, the Monte Carlo parameter errors from these simulations will be automatically used for tracer calculations; these values are red in the `_TrcOut` worksheet—see example 4.

There are more than 250 columns of values that are produced in the output from the `_ModOut` worksheet. Many of the fields are used for documenting the measured concentrations and internal calculations of model components so that results satisfy U.S. Geological Survey (USGS) open data requirements for models.

Environmental Tracer Concentrations

Environmental tracer concentrations can be calculated for every dissolved gas model listed in a `_ModOut` worksheet. This requires that samples have been modeled using the dissolved gas modeling routines listed in the previous section. The tracer calculations are initiated by the “Env. Tracer Calcs” button in the DGMETA tab in the Excel ribbon (fig. 3). The user will be prompted to select a `_ModOut` worksheet (fig. 14A) to calculate tracer concentrations for each dissolved gas model that is listed in the worksheet. The program will match tracer measurements for each corresponding Sample ID and Sample Date listed in the `_ModOut` and `Input_Tracers` worksheets. Calculated tracer concentrations are output to a worksheet named by the user with the suffix “`_TrcOut`” appended to it (fig. 15).

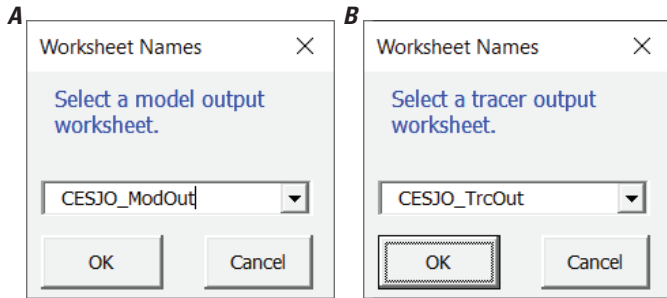


Figure 14. The forms A, for selecting a model output worksheet for computing tracer concentrations and B, for selecting a tracer output worksheet for computing average tracer concentrations (single row per Sample and Date).

Sample Information					Atmospheric Gas Tracers													
Study Unit	Study Area	Sample ID	Sample Date	Record Number / Lab ID	CFC-11 sample, pmol/kg	CFC-11 sample error, pmol/kg	CFC-11, pptv	CFC-11 error, pptv	CFC-12 sample, pmol/kg	CFC-12 sample error, pmol/kg	CFC-12, pptv	CFC-12 error, pptv	CFC-113 sample, pmol/kg	CFC-113 sample error, pmol/kg	CFC-113, pptv	CFC-113 error, pptv	SF6 sample, fmol/kg	
Mixed	UA model	CE-QPC-04	04/06/2006	0060089801	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	UA model	CE-QPC-06	04/19/2006	0060096001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	UA model	MER-01	03/27/2006	0060079501	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	UA model	MER-03	03/30/2006	0060079801	2.931476	0.029315	203.3461	0.601198	40.22293	0.402229	10182.46	2088.255	0.051475	0.000515	11.83432	2.427024	203.346	
Mixed	CE model	MER-05	04/03/2006	0060089501	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-07	04/06/2006	0060089701	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-12	04/13/2006	0060090701	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-14	04/17/2006	0060095501	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-18	04/19/2006	0060095901	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-20	05/01/2006	0060098301	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-22	05/02/2006	0060098701	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MER-23	06/11/2006	0060122001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MERFP-01	04/13/2006	0060091001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MERMW-05	04/05/2006	0060090501	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MOD-04	03/20/2006	0060075901	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MOD-06	03/21/2006	0060076001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	MOD-09	03/23/2006	0060078101	0.263192	0.002632	16.47486	2.770432	0.410751	0.004108	93.51007	15.72477	0.009773	9.77E-05	1.983119	0.333484	16.4748	
Mixed	CE model	MOD-10	05/03/2006	0060099001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	TRLK-02	03/16/2006	0060070101	1.186248	0.011862	87.19091	28.45712	9.343629	0.093436	2461.69	803.4394	0.021001	0.00021	5.098165	1.663924	na	
Mixed	CE model	TRLK-05	03/22/2006	0060078201	0.263588	0.002636	18.53065	3.515296	0.456495	0.004565	116.4881	22.09799	0.018158	0.000182	4.224253	0.801348	na	
Mixed	CE model	TRLK-10	03/27/2006	0060079401	0.353588	0.003536	23.77344	5.271979	0.899181	0.008992	216.2003	47.94442	0.097119	0.000971	21.15456	4.691219	na	
Mixed	CE model	TRLK-11	03/28/2006	0060079601	0.754098	0.007541	52.91269	10.16135	1.784556	0.017846	454.7367	87.32758	0.057888	0.000579	13.4508	2.583091	na	
Mixed	CE model	TRLK-14	04/04/2006	0060089401	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	TRLK-15	04/04/2006	0060089901	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	TRLK-16	05/02/2006	0060099401	na	na	na	na	na	na	na	na	na	na	na	na	na	
Mixed	CE model	TRLKMW-01	03/15/2006	0060070601	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	CE model	CE-QPC-01	03/20/2006	0060079001	141.43	1.4143	10190.19	2033.965	2441.836	24.41836	619920.6	123736.4	0.902463	0.009025	210.716	42.05899	na	
Modern	UA model	CE-QPC-02	03/22/2006	0060076301	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	UA model	CE-QPC-03	03/28/2006	0060079901	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	UA model	CE-QPC-08	05/02/2006	0060098601	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	UA model	CE-QPC-09	05/03/2006	0060099301	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	CE model	MER-02	03/29/2006	0060079701	1.551992	0.01552	129.2536	29.93033	2.447388	0.024474	705.1523	163.2871	0.292677	0.002927	79.99373	18.52358	na	
Modern	CE model	MER-04	03/30/2006	0060080001	na	na	na	na	na	na	na	na	na	na	na	na	na	
Modern	CE model	MER-09	04/10/2006	0060092101	2.550153	0.025502	184.4312	33.75261	305.0375	3.050375	76903.99	14074.14	0.353195	0.003532	82.11032	15.02695	na	
Modern	UA model	MER-10	04/11/2006	0060092201	4.420636	0.044206	292.7859	51.30282	7.786165	0.077862	1873.984	328.3651	1.63231	0.016323	353.9253	62.01587	na	
Modern	CE model	MER-11	04/12/2006	0060090901	0.61058	0.006106	37.69776	6.443332	1.074735	0.010747	228.9505	39.13241	3.266811	0.032668	624.8697	106.8032	na	

Figure 15. The _TrCOut worksheet, which contains calculations of atmospheric dry-air mole fractions and concentrations of tritium-helium-3 components.

_TrcOut Worksheet

The TrcOut worksheet (fig. 15) contains the calculated dry-air mole fractions (mixing ratios) of atmospheric transient gas tracers and concentrations of $^3\text{H-He}$ components for every model listed in the corresponding _ModOut worksheet. Parameter errors that are red are errors computed from Monte Carlo simulations reported in the _ModOut worksheet—see example 4. These errors can be preferred when parameter errors determined from dissolved gas model fits are of the same magnitude as the fitted parameters. In particular, the CE model can have large parameter errors when the F parameter approaches 1.

Details of the methods used for the calculations of tracer concentrations were given in the “Environmental Tracers” section. The $^3\text{He}_{\text{trit}}$ calculations are dependent on the R_{terr} and the _TrcOut worksheet, which provides a graphical approach for evaluating different sources of He_{terr} and their effect on $^3\text{He}_{\text{trit}}$ concentrations. The calculated value of R_{terr} is to the right of the $\delta^3\text{He}$ graph and is blue; that value should be evaluated using the graph (fig. 2) on the _TrcOut worksheet. The R_{terr} can be manually changed by entering a new value in the cell on the _TrcOut worksheet. These parts of the worksheet and functionality are demonstrated in examples 3 and 4.

Formatting

There are two routines in the DGMETA tab that can be used to reformat worksheets created by DGMETA. The first routine, “Collapse Tracer Calcs” can collapse multiple tracer calculations for a single Sample ID and Sample Date, which can be useful for finalizing the reporting of results and transferring them to other programs. The second routine reformats the _ModOut, _TrcOut, and _AvgVal worksheets into a new worksheet with a single-row header that is useful for exporting the results into another program. This output worksheet is in a format that meets USGS model open data requirements for documentation of model inputs and outputs.

If there are multiple dissolved gas models in a _ModOut worksheet or multiple tracer measurements in

the Input_Tracers worksheet for a single Sample ID and Sample Date, the _TrcOut worksheet can contain multiple rows of tracer results for the same Sample ID and Sample Date. Multiple models and tracer measurements may provide additional estimates of uncertainty for the calculated tracer concentrations or identify samples that may be contaminated, degraded, or were collected improperly. The “Collapse Tracer Calcs” button in the DGMETA tab can be used to collapse the multiple rows into a single row for each unique Sample ID and Sample Date. The program will prompt the user (fig. 14B) to select a _TrcOut worksheet and create a new worksheet with a suffix “_AvgVal” appended to the name. The worksheet is organized and formatted the same as the _TrcOut worksheet, but the program will compute the average tracer concentration for multiple tracer results.

_AvgVal Worksheet

This worksheet contains average dissolved gas model results and tracer concentrations for every unique Sample ID and Sample Date reported in the _TrcOut worksheet (fig. 16). The _AvgVal worksheet can be useful for collapsing multiple tracer measurements from different laboratories or for comparing the effect of different dissolved gas model results on tracer concentration calculations. The _AvgVal worksheet should not be used, however, as a sole source of results when reporting the model outcomes. In cases where the dissolved gas models or computed tracer concentrations are very different, the averaging of the results could be undesirable, so users are advised to look closely at the _TrcOut worksheet before averaging the results.

_ModFlt, _TrcFlt, and _AvgFlt Worksheets

Worksheets with the suffix _ModFlt, _TrcFlt, and _AvgFlt are reformatted versions of the _ModOut, _TrcOut, and _AvgVal worksheets (fig. 17). These worksheets are identical to the original worksheets, but contain a single-row header that enable the worksheets and results to be portable to other programs and graphing software.

Study Unit	Study Area	Sample ID	Sample Date	Record Number / Lab ID	SF6 sample, fmol/kg	SF6 sample error, fmol/kg	SF6, pptv	SF6 error, pptv	Tritium, TU	Tritium error, TU	3He/4He sample: R(s), atom ratio	3He/4He sample error, atom ratio	Helium measured: He(s), cm3/g	He error
TX	N2 < 0.5	291949095024801	41541	480130310201	0.149798	0.01498	0.359965	0.12451	-0.0689655	0.03134796	4.51013E-08	1.384E-08	4.4477E-06	4.44
TX	N2 < 0.5	292923095091601	41541	480130310301	0.250474	0.025047	0.537499	0.243137	0.01880878	0.03134796	6.67904E-08	1.384E-08	1.9147E-06	1.914
TX	N2 < 0.5	292944095550101	41493	480130307801	na	na	na	na	-0.1347962	0.03134796	2.43999E-07	1.384E-08	4.225E-07	1.4
TX	N2 < 0.5	300413094402101	41508	480130308501	0.226839	0.022684	0.530518	0.083479	-0.0188088	0.03134796	2.75139E-07	1.384E-08	4.323E-07	31
TX	N2 < 0.5	300932094005301	41540	480130310101	0.119657	0.011966	0.260031	0.122202	0.03761755	0.03134796	2.06078E-07	1.384E-08	9.148E-07	3.3
TX	N2 < 0.5	301420095093201	41507	480130308401	0.970399	0.09704	2.397492	1.01028	-0.0564263	0.03134796	1.18014E-06	1.384E-08	6.57E-08	
TX	N2 < 0.5	302145095473901	41506	480130308201	na	na	na	na	0.01567398	0.03134796	3.52782E-07	1.384E-08	2.344E-07	43
TX	N2 < 0.5	303000095002001	41507	480130308301	0.6578	0.06578	1.536738	0.297582	0.09404389	0.03134796	na	na	na	
TX	N2 < 0.5	304063094101801	41520	480130309001	0.215646	0.021565	0.449388	0.237041	0.02507837	0.03134796	6.97121E-07	1.384E-08	1.178E-07	11
TX	N2 < 0.5	305947093395001	41521	480130309101	0.176185	0.017619	0.347884	0.173657	-0.0721003	0.03134796	4.32638E-07	1.384E-08	2.21E-07	43
TX	N2 > 2	271315097473201	41527	480130309401	0.858352	0.085835	2.266764	0.622268	-0.2225705	0.03134796	1.10858E-07	1.384E-08	8.39E-07	1.6
TX	N2 > 2	271505098073401	41536	480130310001	1.596242	0.159624	4.539481	1.292242	-0.0282132	0.03134796	1.71062E-07	1.384E-08	9.64E-07	0.000
TX	N2 > 2	271843098401101	41535	480130309901	0.120664	0.012066	0.319633	0.107	-0.1473354	0.03134796	4.19106E-08	1.384E-08	4.3878E-06	4.387
TX	N2 > 2	272638098532301	41534	480130309801	4.30572	0.430572	8.621309	2.41713	2.78369906	0.03134796	3.88212E-07	1.384E-08	1.876E-07	11
TX	N2 > 2	274439098144401	41533	480130309701	2.438808	0.243881	6.882279	3.715667	0.03448276	0.03134796	1.3065E-07	1.384E-08	8.176E-07	1.4
TX	N2 > 2	280951096593801	41514	480130308801	0.863902	0.08639	1.849333	2.44515	-0.0532915	0.03134796	1.14042E-07	1.384E-08	1.0221E-06	3.2
TX	N2 > 2	281433097191300	41529	480130309601	0.598857	0.059886	1.501381	0.414791	-0.1128527	0.03134796	na	na	na	
TX	N2 > 2	291639097093901	41512	480130308601	0.460076	0.046008	1.03046	0.277078	-0.0188088	0.03134796	na	na	na	
TX	N2 > 2	302207096050600	41505	480130308101	0.121829	0.012183	0.271911	0.072842	0.02194357	0.03134796	4.28781E-08	1.384E-08	7.3628E-06	7.36
TX	N2 > 2	310935093352701	41522	480130309201	1.261564	0.126156	2.819269	0.756456	1.67711599	0.03134796	1.55728E-06	1.384E-08	7.58E-08	
TX	N2 0.5 - 2	260204097443701	41526	480130309301	2.383688	0.238369	7.441949	2.873889	-0.1159875	0.03134796	1.33902E-06	1.384E-08	5.54E-08	
TX	N2 0.5 - 2	275725097562701	41528	480130309501	2.415467	0.241547	5.687241	1.541646	-0.1943574	0.03134796	na	na	na	
TX	N2 0.5 - 2	284749097503201	41513	480130308701	0.83826	0.083826	1.883382	0.520973	0.04075235	0.03134796	na	na	na	
TX	N2 0.5 - 2	290028095594700	41494	480130307901	0.363841	0.036384	0.806401	0.415751	-0.0971787	0.03134796	6.02455E-07	1.384E-08	1.274E-07	11
TX	N2 0.5 - 2	293938095561301	41492	480130307701	0.305938	0.030594	0.783733	0.351374	-0.0282132	0.03134796	5.34362E-07	1.384E-08	1.516E-07	11
TX	N2 0.5 - 2	294040096542401	41500	480130308001	0.655058	0.065506	1.139536	0.487806	0.00626959	0.03134796	3.34087E-08	1.384E-08	7.2803E-06	7.280

Figure 16. The _AvgVal worksheet, which contains average values of tracer concentrations for each sample and date listed on the _TrcOut worksheet.

	A	B	C	D	E	F	G	H	I	J	K	
1	StudyUnit	StudyArea	SampleID	SampleDate	RecordNum	DG_I_Salinity_permil	DG_I_Elev_masl	DG_I_Temp_C	DG_I_ExcAir_cm3kg	DG_I_Fractionation	DG_I_ExcN2_mgL	
2	TX	N2 < 0.5	291949095024801	41541	480130310201	0.60750158	5.487804878	21	1	0	0	Unf
3	TX	N2 < 0.5	291949095024801	41541	480130312901	0.60750158	5.487804878	21	1	0	0	Unf
4	TX	N2 < 0.5	292923095091601	41541	480130310301	0.605816836	9.146341463	20.87999916	1	0	0	Unf
5	TX	N2 < 0.5	292923095091601	41541	480130313001	0.605816836	9.146341463	20.87999916	1	0	0	Unf
6	TX	N2 < 0.5	292944095550101	41493	480130307801	0.273513002	32.31707317	20.79000092	1	0	0	Unf
7	TX	N2 < 0.5	292944095550101	41493	480130310501	0.273513002	32.31707317	20.79000092	1	0	0	Unf
8	TX	N2 < 0.5	300413094402101	41508	480130308501	0.706403541	19.81707317	20.15999985	1	0	0	Unf
9	TX	N2 < 0.5	300413094402101	41508	480130311201	0.706403541	19.81707317	20.15999985	1	0	0	Unf
10	TX	N2 < 0.5	300932094005301	41540	480130310101	0.310427655	7.926829268	20.01000023	1	0	0	Unf
11	TX	N2 < 0.5	300932094005301	41540	480130312801	0.310427655	7.926829268	20.01000023	1	0	0	Unf
12	TX	N2 < 0.5	301420095093201	41507	480130308401	0.223762018	39.02439024	20.09000015	1	0	0	Unf
13	TX	N2 < 0.5	301420095093201	41507	480130311101	0.223762018	39.02439024	20.09000015	1	0	0	Unf
14	TX	N2 < 0.5	302145095473901	41506	480130308201	0.371431295	92.07317073	20.09000015	1	0	0	Unf
15	TX	N2 < 0.5	302145095473901	41506	480130310901	0.371431295	92.07317073	20.09000015	1	0	0	Unf
16	TX	N2 < 0.5	303000095002001	41507	480130308301	0.317700797	50.30487805	19.70000076	1	0	0	Unf
17	TX	N2 < 0.5	303000095002001	41507	480130311001	0.317700797	50.30487805	19.70000076	1	0	0	Unf
18	TX	N2 < 0.5	304603094101801	41520	480130309001	0.148916404	61.58536585	19.21999931	1	0	0	Unf
19	TX	N2 < 0.5	304603094101801	41520	480130311701	0.148916404	61.58536585	19.21999931	1	0	0	Unf
20	TX	N2 < 0.5	305947093395001	41521	480130309101	0.120449445	61.58536585	18.95000076	1	0	0	Unf
21	TX	N2 < 0.5	305947093395001	41521	480130311801	0.120449445	61.58536585	18.95000076	1	0	0	Unf
22	TX	N2 > 2	271315097473201	41527	480130309401	1.041121567	10.67073171	22.43000031	1	0	0	Unf
23	TX	N2 > 2	271315097473201	41527	480130312101	1.041121567	10.67073171	22.43000031	1	0	0	Unf
24	TX	N2 > 2	271505098073401	41536	480130310001	0.681666318	37.80487805	22.64999962	1	0	0	Unf
25	TX	N2 > 2	271843098401101	41535	480130309901	1.253733684	168.2926829	22.43000031	1	0	0	Unf
26	TX	N2 > 2	271843098401101	41535	480130312601	1.253733684	168.2926829	22.43000031	1	0	0	Unf
27	TX	N2 > 2	272638098532301	41534	480130309801	1.039992178	247.5609756	22.23999977	1	0	0	Unf
28	TX	N2 > 2	272638098532301	41534	480130312501	1.039992178	247.5609756	22.23999977	1	0	0	Unf
29	TX	N2 > 2	274439098144401	41533	480130309701	0.816691643	98.7804878	22.39999962	1	0	0	Unf
30	TX	N2 > 2	274439098144401	41533	480130312401	0.816691643	98.7804878	22.39999962	1	0	0	Unf
31	TX	N2 > 2	280951096593801	41514	480130308801	2.137940975	1.829268293	22.02000046	1	0	0	Unf
32	TX	N2 > 2	280951096593801	41514	480130311501	2.137940975	1.829268293	22.02000046	1	0	0	Unf
33	TX	N2 > 2	281433097191300	41529	480130309601	0.798111863	12.80487805	21.82999992	1	0	0	Unf
34	TX	N2 > 2	281433097191300	41529	480130312301	0.798111863	12.80487805	21.82999992	1	0	0	Unf
35	TX	N2 > 2	291639097093901	41512	480130308601	0.568761664	81.70731707	20.79000092	1	0	0	Unf
36	TX	N2 > 2	291639097093901	41512	480130311301	0.568761664	81.70731707	20.79000092	1	0	0	Unf
37	TX	N2 > 2	302207096050600	41505	480130308101	0.59795177	61.8902439	20.02000046	1	0	0	Unf
38	TX	N2 > 2	302207096050600	41505	480130310801	0.59795177	61.8902439	20.02000046	1	0	0	Unf
39	TX	N2 > 2	310935093352701	41522	480130309201	0.064662381	64.63414634	18.79999924	1	0	0	Unf
40	TX	N2 > 2	310935093352701	41522	480130311901	0.064662381	64.63414634	18.79999924	1	0	0	Unf
41	TX	N2 0.5 - 2	260204097443701	41526	480130309301	0.6153642	17.98780488	23.48999977	1	0	0	Unf
42	TX	N2 0.5 - 2	260204097443701	41526	480130312001	0.6153642	17.98780488	23.48999977	1	0	0	Unf

Figure 17. A _ModFit worksheet, which is a single-row header version of a _ModOut, _TrcOut, or _AvgVal worksheet.

Examples

The following examples provide guidance for entering and comparing different solubility equations, strategies for modeling dissolved gas concentrations with a limited set of measured gases, the identification of mantle He in groundwater, and samples that have been degassed. This is not a comprehensive set of examples to show the full capability of the program. All figures included in the examples were created using the DGMETA workbooks that are included in the DGMETA installation package. Users are encouraged to use them while following the written examples below.

Example 1—Comparison of Noble Gas Solubility Data in Freshwater and Seawater

DGMETA includes multiple solubility data for each noble gas—see the Database worksheet for the list of gases. For most noble gases, the solubilities from different studies vary less than 1 percent over temperatures between 0 and 40 °C and salinities between 0 and 35 per mil. However, the solubility of Ne among studies frequently varies by more than 1 percent over this range of temperature and salinity (fig. 18).

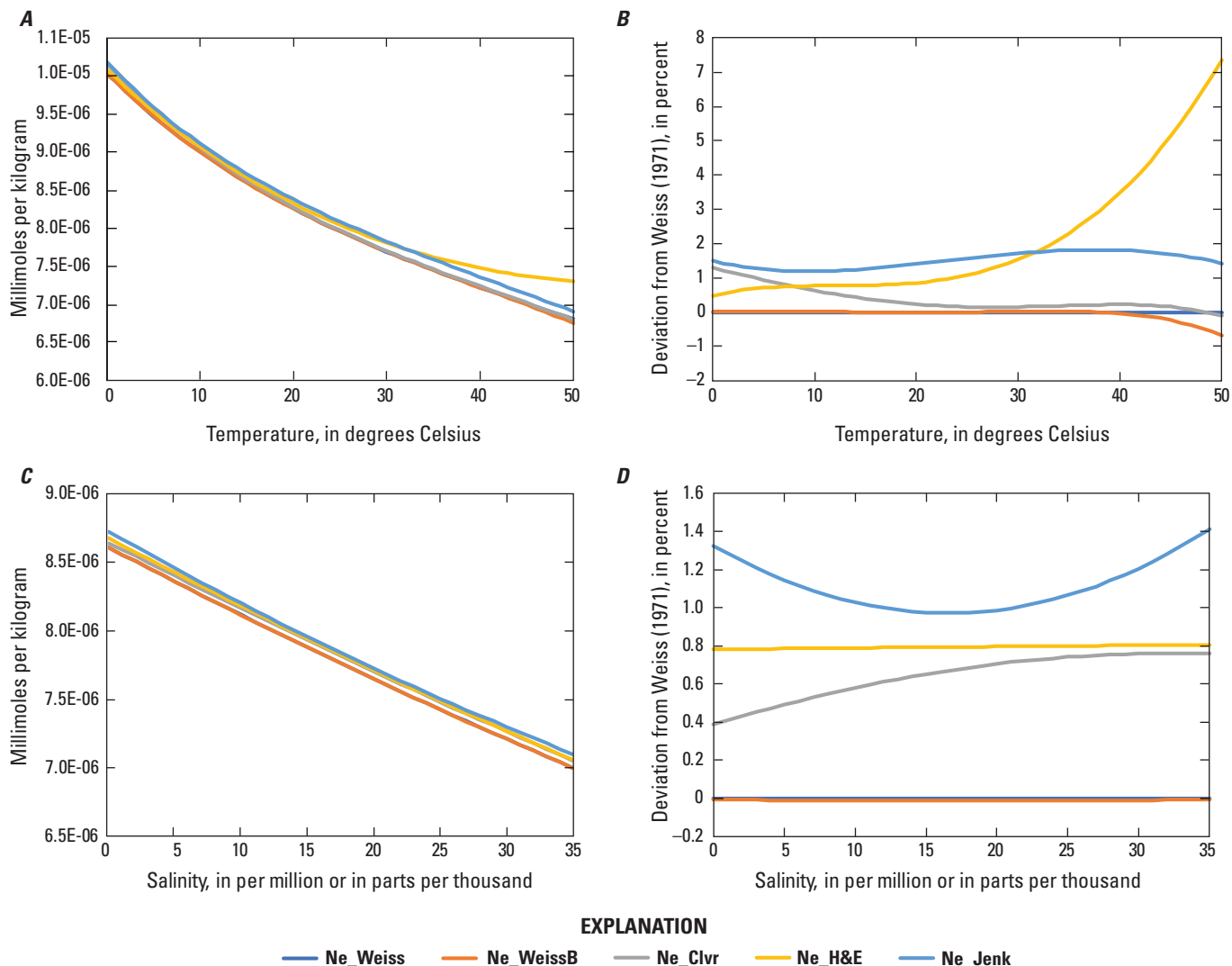


Figure 18. Neon (Ne) concentrations in freshwater and saltwater at equilibrium with air, based on solubility equations by Weiss (1971) that were expressed as the moist-air solubility (Ne_Weiss) and Bunsen solubility constant (Ne_WeissB), by Clever (1979a; Smith and Kennedy, 1983; Ne_Clvr), by Hamme and Emerson (2004; Ne_H&E), and by Jenkins and others (2019; Ne_Jenk). *A*, variation in neon solubility concentrations in freshwater (salinity = 0 per mil) over the temperature range of 0–50 °C; *B*, deviation of the solubility concentrations derived from all four equations compared to those derived from the gravimetric equation of Weiss (1971) as a function of temperature; *C*, variation of neon solubility concentrations at a temperature of 15 °C over the salinity range of 0–35 per mil; and *D*, deviation of the solubility equations from those of the gravimetric equation of Weiss (1971) as a function of salinity. The names of the lines consist of the name of the gas and a descriptor of the reference for the source of the gas solubility data and are unique identifiers for the gas solubility data used by DGMETA (see the Database worksheet of DGMETA).

DGMETA includes solubility data for Ne in freshwater and seawater from five studies. These solubility data were graphed using the “Gas Solubilities” routine in the DGMETA tab (fig. 3) and selecting the Ne solubilities listed in the Gas Solubilities form (fig. 8). In general, these studies measured the solubility of Ne in freshwater and seawater over a range of temperatures and fit polynomial equations to the experimental solubility data. The derived expressions provide a reasonable approximation of the solubility of the gas in water as a

function of temperature and salinity for the conditions used in each experiment. Many of the studies used different methods and instruments to measure the solubility. The purpose of the analysis presented here is to compare the differences in solubility to evaluate their applicability over a range of environmental conditions rather than a detailed examination and comparison of the methods used to develop the solubility functions or to identify a “correct” set of solubility equations.

Weiss (1971) provided two equations for the solubility of Ne: (1) one equation based on the moist-air solubility at 1 atm (Ne_Weiss) and (2) another equation for the Bunsen solubility (Ne_WeissB). Both equations used the van 't Hoff equation and Setchénov relation for solubility and salinity corrections (G_1). Clever (1979a) determined the solubility of Ne in water in terms of the mole fraction solubility at standard pressure (1 atm) from a compilation of several solubility studies, and these solubility equations were combined with salting coefficients for solutions of NaCl (0.0–5.2 mol/L) computed by Smith and Kennedy (1983; G_3). Hamme and Emerson (2004) reexamined the solubility of Ne (G_5) using the equations of Garcia and Gordon (1992; G_5). Most recently, Jenkins and others (2019) performed solubility experiments for Ne in freshwater and seawater and reported their solubility using a modified version of the Weiss (1970) equation to include an additional salinity term introduced by Garcia and Gordon (1992; G_6). These five solubility equations can be easily compared in DGMETA by clicking the “Gas Solubility” button on the DGMETA tab (see the “Graphing” section).

The Weiss solubility equations are the default or primary solubility equations used by the program because the experiments used to derive the equations were done over a wide range of temperatures and salinities using the same or similar methods for each gas. The Weiss solubility for Ne was reported in terms of volumetric Bunsen coefficients (Ne_WeissB) and gravimetric moist air solubilities (Ne_Weiss). Deviations between the two forms are less than 0.04 percent over the temperature range of 0–40 °C (figs. 18A, B). The solubilities derived from the mole-fraction-based equations of Clever (1979a) for freshwater (Ne_Clvr) deviate from the Weiss solubilities usually less than 2 percent, whereas solubilities from Hamme and Emerson (2004; Ne_H&E) are more than 0.5 percent higher than the Weiss solubilities over the entire temperature range (figs. 18A, B). The Jenkins (2019) solubilities for Ne in freshwater were more than 1 percent over the entire temperature range. At temperatures greater than 30 °C, Hamme and Emerson (2004) solubilities grow to more than 2 percent because their experiments were done for the temperature range of 0–25 °C and seawater experiments for the temperature range of 0–30 °C. Solubility equations determined by Clever (1979a, b, 1980) were fit to several reported sets of measured solubility equations over the temperature range of 5–66 °C. For temperatures less than 5 °C, this may partly explain deviations between the Clever and Weiss solubilities. It should be noted that the Clever solubilities for He, Ar, and Kr were partly based on solubility data from Weiss; and therefore, the Clever solubilities can be similar to the Weiss solubilities.

These differences highlight the importance of choosing solubility equations best suited to the environmental conditions being studied. For freshwater terrestrial environments, the Weiss solubilities combined with Xe

solubility from Clever (1979b) and Smith and Kennedy (1983) are commonly used. Newer solubility studies by Hamme and Emerson (2004) and Jenkins (2019) may be more common in oceanographic or saltwater studies.

Hamme and Emerson (2004) noted that small inaccuracies of the solubility equations can lead to large differences in biological fluxes of O_2 production. In their study, they showed that the most commonly used solubility data for Ne in freshwater and seawater was most often lower, about 1 percent or more, than the solubility of Ne they determined (Ne_H&E; figs. 18B, D). In particular, the Weiss solubilities had the highest deviations. Sano and Takahata (2005) measured equilibrium concentrations of noble gases in seawater for nine temperatures ranging from 1 to 29.6 °C. The measured Ne data were compared to Ne concentrations predicted from the Ne_Weiss, Ne_Clvr, Ne_H&E, and Ne_Jenk solubilities. Figure 19 shows the percentage of deviation from the measured data reported by Sano and Takahata (2005). The Weiss solubility of Ne were lower than the measured data for the entire temperature range and were more than 1 percent lower for many temperatures. Almost all of the predicted Ne were lower than the measured Ne for temperatures greater than 15 °C. Neon from Ne_H&E, Ne_Clvr, and Ne_Jenk were most similar to the Ne data from Sano and Takahata (2005) and indicate that those solubilities may be better suited for oceanographic studies.

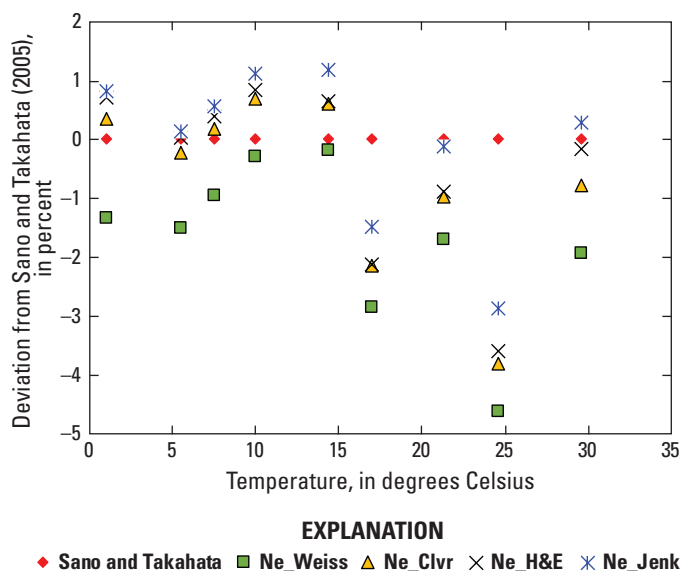


Figure 19. Percentage of deviation of neon (Ne) solubility from measured data reported by Sano and Takahata (2005) in seawater (salinity equals 34.2 per mil) for a range of temperatures. The names of the points consist of the name of the gas and a descriptor of the reference for the source of the gas solubility data and are unique identifiers for the gas solubility data used by Dissolved Gas Modeling and Environmental Tracer Analysis (DGMETA; see the Database worksheet of DGMETA).

Despite the differences in Ne solubility, overall differences in gas solubilities are usually less than 1 percent among all types of water. Solubility equations can be chosen to maximize precision for specific temperature and salinity conditions. Most solubility equations are valid for temperatures between 0 and 40 °C and salinity from 0 to 35 per mil, although individual solubility equations may have broader or shorter temperature and salinity ranges based on the experimental data used to derive the solubility equation.

Example 2—Inverse Modeling of Air-Equilibrated Freshwater and Seawater Samples

A common application of measuring noble gases in water is to determine the temperature of the water when it equilibrated with the atmosphere. The temperature is determined by inverse modeling of the measured noble gas concentrations with modeled concentrations predicted by solubility. The noble gas concentrations reported by Sano and Takahata (2005) were from nine seawater samples equilibrated with air at different temperatures. Inverse modeling of the measured concentrations should, in theory, predict the air-water equilibration temperature of each sample in the

experiment (1, 5.5, 7.5, 10, 14.4, 17, 21.3, 24.6, and 29.6 °C). Similarly, the USGS Noble Gas Laboratory in Denver, Colorado, routinely prepares air-equilibrated distilled-water (AEW) samples for laboratory quality-assurance purposes (Hunt, 2015). Between April 2016 and August 2017, the USGS Noble Gas Laboratory prepared 51 AEW samples that were equilibrated with room air at about 20 °C.

The temperatures of these air-equilibrated water and seawater samples were modeled using the full suite of measured noble gases using different sets of solubility. The default set used the Weiss solubilities for He, Ne, Ar, and Kr, and the solubility of Xe from Clever (1979b) and Smith and Kennedy (1983). The second set used the solubility equations from Clever (1979a, b, 1980) and Smith and Kennedy (1983). The third set used the solubility of Ar and Ne from Hamme and Emerson (2004), He from Weiss (1971), Kr from Weiss and Kyser (1978), and Xe from Clever (1979b) and Smith and Kennedy (1983). The fourth set used the solubility of noble gases reported by Jenkins and others (2019). The Dissolved Gas Modeling form was configured to find the temperature of AEW and seawater samples at air-water equilibrium for each set of noble gas solubilities (fig. 20). For the USGS Noble Gas Laboratory AEW samples, He was not modeled because a known source of excess atmospheric He at the USGS Noble Gas Laboratory contaminated the AEW samples.

1. Select samples to model

Sample ID	Row Num
AEW #16	41
AEW #21 4/24/17	42
AEW #24	43
AEW #30	44
AEW #5	45
AEW #9	46
AEW#18 4/24/17	47
AEW #21	48
AEW #26	49
AEW #5	50
AEW #1	51
AEW #2	52
AEW #7	53
AEW #8	54
SW-#7_1_C	55
SW-#8_5.5_C	56
SW-#1-6_7.5_C	57
SW-#9_10_C	58
SW-#10_14.4_C	59
SW-#11_17_C	60
SW-#12_21.3_C	61
SW-#13_24.6_C	62

Model all samples

2. Select gases to model

- He, cm³/g
- Ne, cm³/g
- Ar, cm³/g
- Kr, cm³/g
- Xe, cm³/g
- N₂, cm³/g
- Ar, mg/L
- N₂, mg/L
- O₂, mg/L
- CO₂, mg/L
- CH₄, mg/L
- H₂, mg/L
- N₂O, mg/L

3. Select parameters to model

- Temperature
- Excess air
- Salinity
- Elevation / pressure
- Fractionation (excess air)
- Excess nitrogen gas

4. Select models and options

Models

- Unfractionated excess air (UA)
- Partial re-equilibration (PR)
- Closed-system equilibration (CE)

Model options

- Use alt. search method
- Rerun bad fits with reduced gases
- Calculate excess nitrogen gas
- Run Monte Carlo simulations
- Excess N₂ for Ar/N₂ only

5. RUN MODELS **CLOSE FORM**

Figure 20. The Dissolved Gas Modeling form used to evaluate air-equilibrated samples prepared at the U.S. Geological Survey (USGS) Noble Gas Laboratory in Denver, Colorado, and seawater samples from Sano and Takahata (2005). Helium was not included in dissolved gas model fits for air-equilibrated, distilled-water samples from the USGS Denver Noble Gas Laboratory.

Results of the dissolved gas modeling for seawater samples showed that none of the four sets of solubility data fit the seawater sample data well. It also was counterintuitive that the modeled temperature agreed more with the reported temperature for the sets of solubilities with poorer fits than for sets of solubilities with better fits. The median chi-square probabilities were 3.2, 12, 18.4, and 14.5 percent for the Weiss, Clever, Hamme, and Jenkins solubilities, respectively. Temperature agreements, measured by the median of the percent deviation from the reported temperature, were -0.24 , 0.04 , -1.5 , and -4.4 percent for the Weiss, Clever, Hamme, and Jenkins solubilities, respectively. Despite some poor fits to the data, the modeled temperatures were generally within 0.5 °C of the reported equilibrated temperature.

Results of the dissolved gas modeling for AEW samples prepared by the USGS Noble Gas Laboratory showed that all sets of solubilities fit the measured data well. Unlike the seawater samples, the sets of solubilities with better fits also had better temperature agreement. The median chi-square probabilities were 80.8, 77.8, 76.5, and 70.7 percent for the Weiss, Clever, Hamme, and Jenkins solubilities, respectively. Temperature agreements, measured by the median of the percent deviation from the equilibration temperature of 20 °C, were -0.73 , -0.76 , -1.1 , and -2.9 percent for the Weiss, Clever, Hamme, and Jenkins solubilities, respectively. Temperature disagreements were within 0.5 °C for most of the fits.

Overall, the solubility comparisons for AEW and seawater samples indicate that the Weiss and Clever solubilities may perform better than other solubilities when estimating air-water equilibration temperatures. These solubilities gave better fits to the measured freshwater AEW samples and had better temperature agreements than other solubilities. Although the Weiss and Clever solubilities gave poorer fits to the seawater samples than other solubilities, the Weiss and Clever solubilities gave better temperature agreement. This interesting result could reflect the complexities and difficulties in the preparation and measurement of gases in concentrated salt solutions. Although the analysis of modeled fits to AEW samples and seawater support the use of the Weiss data and the Clever data for Xe for most applications, the data used in this comparison were not rigorously assessed, and comparisons to other data or to data collected over a different range of temperatures may support other sets of solubility equations. Therefore, users are given the option to substitute different solubility equations and parameters to explore dissolved gas model fits and results for temperature and excess air.

Example 3—Dissolved Gas Modeling with Neon, Argon, and Nitrogen or Argon and Nitrogen

This example shows how data from different labs can be combined to model recharge temperatures and excess air in an aquifer where denitrification complicates the interpretation. Samples where denitrification has increased the amount of dissolved N_2 gas can make it difficult to determine temperature and excess air from Ar and N_2 concentrations alone or from Ar, N_2 , and Ne concentrations. In this situation, the temperature, excess air, and excess N_2 need to be determined; but in one case only two gases are available and in the other case Ne, Ar, and N_2 are available. This situation is best solved by working with samples that have Ar, N_2 , and Ne data first to provide ranges of possible temperatures and excess air and then to use those estimates to inform the modeling of samples with Ar and N_2 only.

Water samples for analysis of N_2 and Ar were collected from 26 wells in the Texas coastal lowlands aquifer in August and September 2013. These samples were measured at the USGS Groundwater Dating Laboratory (Reston, Virginia) using gas chromatography (U.S. Geological Survey, 2020) and were reported in mg of gas per L of water. Samples from a subset of 19 wells were analyzed for He, Ne, and $\delta^3\text{He}$ at the Lamont-Doherty Earth Observatory (Ekwurzel and others, 1994; Ludin and others, 1998). Five of the 19 samples were analyzed at the USGS Noble Gas Laboratory in Denver, Colorado (Hunt, 2015). Concentrations of He and Ne were reported in units of cm^3 of gas at an STP per g of water. DGMETA can handle gases reported in different units and can convert them to common units for graphical display of the data and for inverse modeling of recharge temperature, excess air, and excess N_2 .

Graphs of N_2 concentration versus the Ar-to-Ne ratio and N_2 versus Ar concentrations were made to identify patterns in temperature, excess air, and excess N_2 that could be caused by denitrification in the aquifer (fig. 21). These graphs show that groundwater likely was recharged at temperatures between 10 and 20 °C and had excess air values between 1 and 3 cm^3/kg . Samples that may have been affected by denitrification tend to plot above samples unaffected or less affected by denitrification. Samples affected by denitrification are orange and green on figure 21; samples that are green have excess N_2 between 0.5 and 2 mg/L as N, and samples that are orange have excess N_2 greater than 2 mg/L as N. Samples that are blue on figure 21 have little to no excess N_2 and plot near lower excess air concentrations, typically between 2 and 4 cm^3/kg . The temperature ranges and trends of samples are more consistent on the Ar- N_2 graph than the Ar/Ne- N_2 graph because the concentrations were measured from the sample bottle and used the same analytical method.

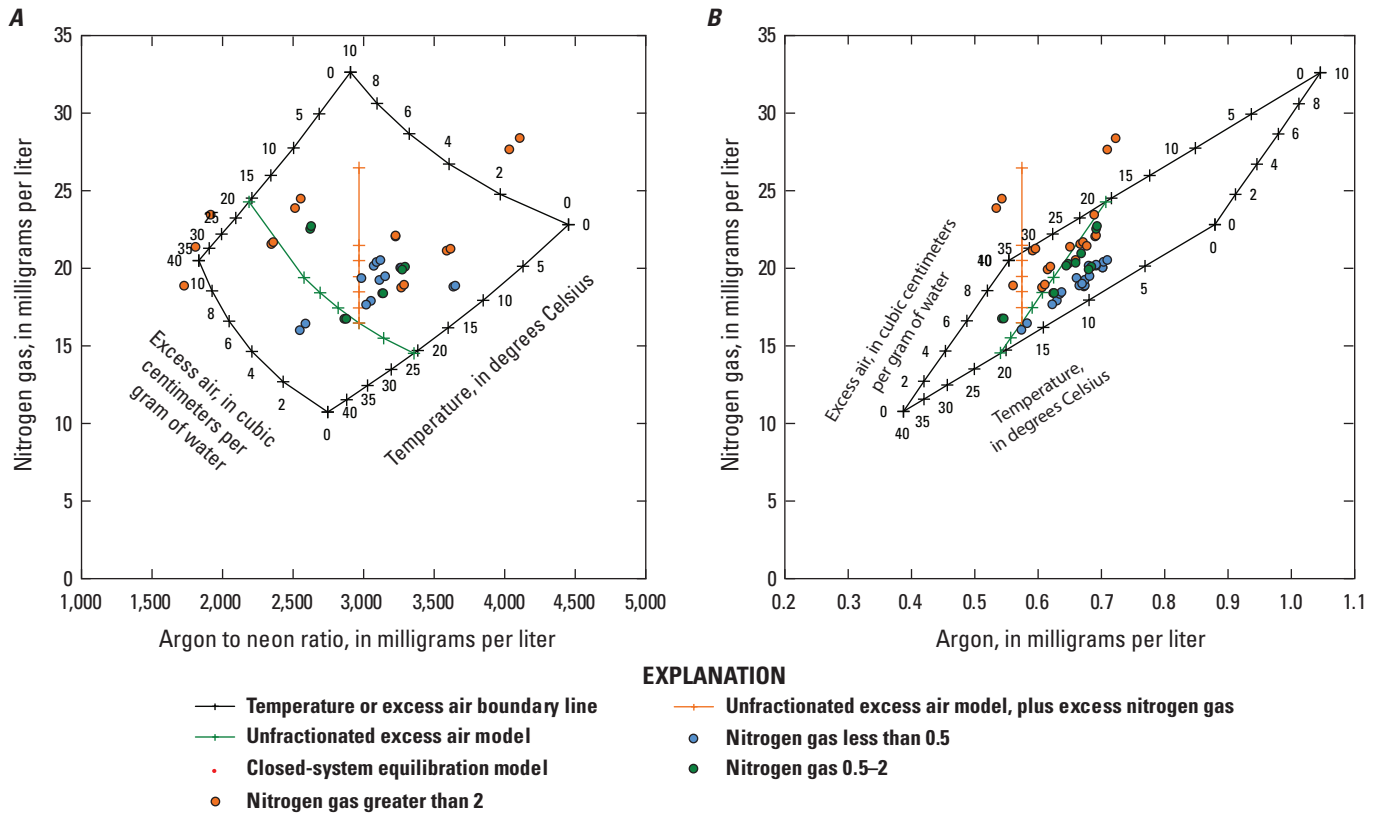


Figure 21. Concentrations of *A*, Nitrogen gas (N_2) and argon and neon ratio, and *B*, N_2 and argon only were measured in groundwater samples from the Texas coastal lowlands aquifer in 2013. Samples are color coded for the amount of excess N_2 (presumably from denitrification; milligrams per liter as nitrogen) determined from graphical analysis and model fits to the data.

In order to assess the extent of potential denitrification, 19 sites with measured values of Ne, Ar, and N_2 were modeled first using the UA model with fit parameters of temperature, excess air, and excess N_2 (fig. 22). Model results indicate that most samples had temperatures around 16 °C (median of samples), excess air of about 2.5 cm^3/kg , and denitrification of about 0.6 mg/L. In some cases, modeled recharge temperatures were too low (8 °C) or too high (42 °C) because the Ne did not agree well with measured Ar and N_2 results. These samples and other samples with near-zero excess air were reevaluated using Ar and N_2 only. Recharge conditions from models that include Ne may differ from Ar- N_2 recharge conditions because of different sample collection techniques that lead to different chemistry of samples, or from denitrification, or biogenic- CH_4 production that causes partial gas loss.

As a next step, all the samples were modeled again using Ar and N_2 only, with fit parameters of temperature and

excess nitrogen gas. The option “Excess N_2 for Ar/ N_2 only” will generate multiple models for a range of excess air values specified on the user form (fig. 23). For each model generated, the best-fit temperature and excess N_2 values are computed and the average temperature, excess N_2 , and excess air value are reported. The median excess air concentration using Ne, Ar, and N_2 was 2.5 cm^3/kg and most models with no excess or a minimal amount of excess N_2 had excess air between 1.5 and 3.5 cm^3/kg . Consequently, a range of 1.5–3.5 cm^3/kg was used as an estimate of excess air in groundwater that likely had undergone denitrification.

The option “Excess N_2 for Ar/ N_2 only” method works best when all samples are from the same aquifer and were recharged under similar conditions. If there are large differences in recharge conditions in an aquifer, this method may overestimate or underestimate the contribution of denitrification to samples.

The screenshot shows the 'Dissolved Gas Modeling' window with four main sections:

- 1. Select samples to model:** A table with columns 'Sample ID' and 'Row Num'. A checkbox 'Model all samples' is checked. The table lists 25 samples, with rows 4 through 25 highlighted in blue.
- 2. Select gases to model:** A list of gases with checkboxes: He, cm3/g; Ne, cm3/g; Ar, cm3/g; Kr, cm3/g; Xe, cm3/g; N2, cm3/g; Ar, mg/L; N2, mg/L; O2, mg/L; CO2, mg/L; CH4, mg/L; H2, mg/L; N2O, mg/L. Ne, Ar, and N2 are selected.
- 3. Select parameters to model:** A list of parameters with checkboxes: Temperature (checked), Excess air (checked), Salinity (unchecked), Elevation / pressure (unchecked), Fractionation (excess air) (unchecked), Excess nitrogen gas (checked).
- 4. Select models and options:**
 - Models:** Unfractionated excess air (UA) (checked), Partial re-equilibration (PR) (unchecked), Closed-system equilibration (CE) (unchecked).
 - Model options:** Use alt. search method (unchecked), Rerun bad fits with reduced gases (unchecked), Calculate excess nitrogen gas (unchecked), Run Monte Carlo simulations (unchecked), Excess N2 for Ar/N2 only (unchecked).

Buttons at the bottom include '5. RUN MODELS' and 'CLOSE FORM'.

Figure 22. The form for Dissolved Gas Modeling for modeling recharge conditions and denitrification using neon (Ne), argon (Ar), and nitrogen gas (N₂) concentrations. In this example, all samples will be modeled using available Ne, Ar, and N₂. Temperature, excess air, and excess N₂ are the parameters to be used to fit the dissolved gas models to the sample data. Elevation and salinity will be specified from the Input_Gases worksheet.

The screenshot shows the 'Dissolved Gas Modeling' window with the same layout as Figure 22, but with additional options selected:

- 2. Select gases to model:** Ar, mg/L and N2, mg/L are also selected.
- 4. Select models and options:**
 - Models:** Unfractionated excess air (UA) (checked), Partial re-equilibration (PR) (unchecked), Closed-system equilibration (CE) (unchecked).
 - Model options:** Use alt. search method (unchecked), Rerun bad fits with reduced gases (unchecked), Calculate excess nitrogen gas (unchecked), Run Monte Carlo simulations (unchecked), Excess N2 for Ar/N2 only (checked).
 - Excess air range, cm³/kg:** A range of 1.5 to 3.5 is specified.

Buttons at the bottom include '5. RUN MODELS' and 'CLOSE FORM'.

Figure 23. The form for Dissolved Gas Modeling for modeling recharge conditions with denitrification using argon (Ar) and nitrogen gases (N₂) only. The option “Excess N₂ for Ar/N₂ only” will compile a list of models that have excess air values between the range specified by the user, 1.5–3.5 cubic meters per kilogram (cm³/kg) in this case, and will report the corresponding concentrations of excess N₂ (presumably from denitrification).

For samples with multiple models of dissolved gas results, the output from each model should be evaluated against one another to select a single dissolved gas model that best describes the set of measured gas concentrations. For this example, selected models are included in the example file and each sample was categorized in the study area column according to the excess N_2 concentration of the chosen model. In general, models with Ne, Ar, and N_2 were preferred over models that used only Ar and N_2 when the excess air was greater than 1 or less than or equal to 6 mg/L as N. In a few instances, the Ne was not useful for determining temperatures and excess air. The final set of models listed in the worksheet called TX_Final_ModOut (in the example workbook) was used to make graphs on figure 21. In this example, the dissolved gas models that were derived based on Ne, Ar, and N_2 , provided the range of likely recharge temperatures, excess air, and extent of denitrification in the aquifer. This information was then used to inform samples with Ar and N_2 data only. Samples with larger excess air values than the range typical of samples with Ne, Ar, and N_2 were likely to have excess N_2 present. In these cases, the UA model was run with a different amount of excess N_2 (entered on the Input_Gases worksheet) until the excess air or temperature ranges were similar to those determined using Ne, Ar, and N_2 .

Combining data from different sample collection types and analytical methods can highlight some of the sources of uncertainty in the laboratory results and the assumptions that underlie the models. Böhlke and others (2007) compared model results using Ar and N_2 (only) with model results using Ne, Ar, and N_2 for an aquifer in Nebraska receiving irrigation recharge. The modeling approach that included Ne data indicated variation in recharge temperature and excess air (assumed to be unfractionated, using the “UA” model). After accounting for those variations, oxic samples had a mean calculated excess N_2 concentration of -6 plus or minus 9 micromoles per L ($\mu\text{mol/L}$) as N (-0.1 mg/L), indicating a minor bias that might have resulted from combining data from different sample collection types and analytical methods. Similar comparisons of calculated excess air in oxic samples for an aquifer in Long Island, New York (Böhlke and others, 2009), yielded a mean excess N_2 value of -14 plus or minus 11 $\mu\text{mol/L}$ as N (0.2 mg/L) when calculated using all three gases. These negative values were interpreted as an indication of uncertainty in the estimation of excess N_2 from such data.

Tracer concentrations for the Texas samples were computed for the final set of dissolved gas models listed in the TX_Final_ModOut worksheet. In this example, concentrations of SF_6 , 3H , and $^3He_{\text{trit}}$ were calculated using the “Env. Tracer

Calcs” button in the toolbar. As part of the $^3He_{\text{trit}}$ computation, the $^3He/^4He$ ratio of He_{terr} was determined automatically by DGMETA. The calculated best-fit line explains the δ^3He evolution of tritium-dead samples. In this example, the best-fit R_{terr} value was 4.43×10^{-8} and is listed in the blue cell in the table to the right of the graph (fig. 24). This value is very similar to the radiogenic helium line (2×10^{-8} ; black dashed line) but is slightly elevated probably because the amount of He in some samples appears to be overestimated from dissolved gas models that do not fit the He data well. In this case, the authors decided to replace the R_{terr} value in the blue cell to the right of the graph with 2×10^{-8} and the best-fit value was ignored.

Average concentrations of the tracers and their errors can be computed as a final step using the “Collapse Tracer Calcs” button in the toolbar. In this study area, SF_6 concentrations above 1.0 volume of gas per volume of dry air, in parts per trillion (pptv), in samples with low 3H (less than 0.5 TU) indicate that SF_6 was contaminated, likely by terrigenic sources or perhaps from atmospheric contamination during sample collection, storage, or shipping. The contamination bias can be identified from a graph of 3H and SF_6 (fig. 25). Because SF_6 is a tracer of water that entered an aquifer after about 1975 or later, groundwater recharged after that date should contain SF_6 concentrations between 0.5 and 9 pptv and have detectable levels of 3H (greater than 0.5 TU). However, 3H concentrations in most samples were less than 0.1 TU, which indicates most of the groundwater was recharged before about 1950, such that all SF_6 concentrations of environmental origin should be below about 0.5 pptv (gray-shaded area in fig. 25). Assuming the laboratory analyses were reliable and sample collection procedures were followed correctly, groundwater samples with SF_6 concentrations above 0.5 pptv and 3H concentrations less than 0.1 TU indicate the introduction of SF_6 from a terrigenic source of SF_6 —diffused from igneous or volcanic rocks (Busenberg and Plummer, 2000; red-shaded area in fig. 25). On the other hand, contamination from exposure to atmospheric sources of SF_6 during sample collection, storage, or shipping could be another explanation. By comparison, the atmospheric mole fraction concentration of SF_6 is about 10 pptv. Sulfur hexafluoride concentrations substantially above the atmospheric levels would indicate a terrigenic source was more likely. Unfortunately, the presence of terrigenic SF_6 can limit the utility of SF_6 for dating water because it may not be possible to tell if the SF_6 was derived from terrigenic or atmospheric sources even when the concentrations are at expected environmental levels.

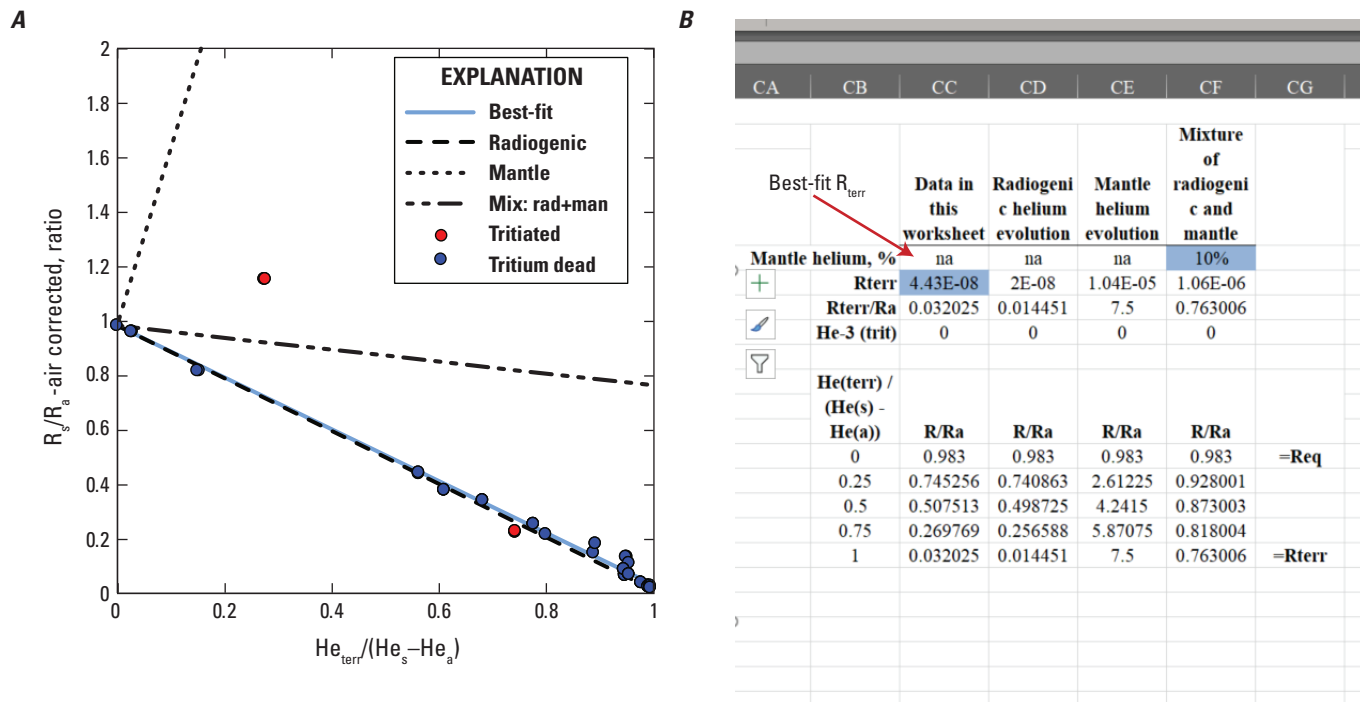


Figure 24. The A, helium isotope separation plot and B, table of helium isotope control variables on the TX_Final_TrcOut worksheet. Dissolved Gas Modeling and Environmental Tracer Analysis automatically calculates a best-fit line for samples with tritium less than 0.5 tritium unit in order to compute the helium-3/helium-4 of terrigenous helium (R_{terr}), which is output in the blue cell to the right of the graph on the _TrcOut worksheet.

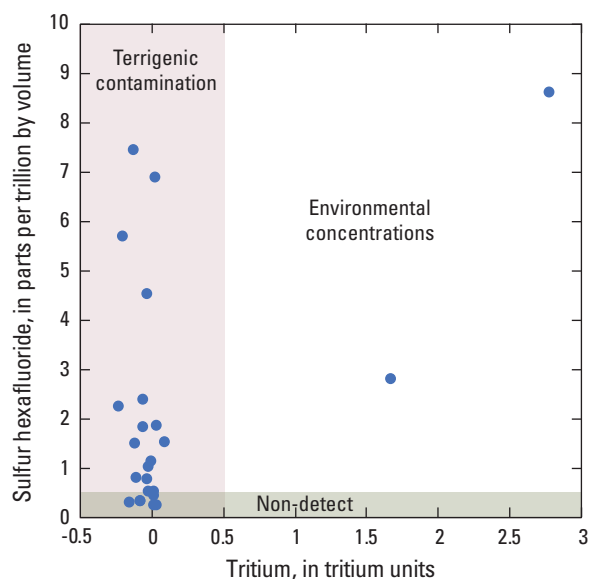


Figure 25. Tritium and sulfur hexafluoride (SF_6) concentrations in groundwater in the Texas coastal lowlands aquifer. Sulfur hexafluoride concentrations below the tritium cutoff line at 0.5 tritium unit (TU) are indicative of terrigenous sources whereas SF_6 concentrations greater than 0.5 TU generally reflect expected environmental concentrations. The presence of terrigenous SF_6 may limit the utility of SF_6 for determining ages of water.

Example 4—Tritogenic Helium-3 Analysis in the Central Eastside San Joaquin Valley, California

The following example shows how dissolved gas modeling and environmental tracer concentrations were determined for a set of samples used for determining age distributions of groundwater in wells in the central eastside of the San Joaquin Valley, California (Green and others, 2016; Jurgens and others, 2016). Even though measurements of noble gases typically provide the best way to determine air-water equilibrium conditions (for example, the temperature and excess air of recharge) in an aquifer, the data from this example do not provide strong evidence that one dissolved gas model is the best choice for determining recharge conditions. Example 4 also demonstrates the importance of Monte Carlo simulation methods for determining parameter uncertainty from CE models. Samples of dissolved gases were modeled using Ne, Ar, Kr, and Xe concentrations and the UA (fig. 26A) and CE models (fig. 26B). To evaluate the results of the dissolved gas models, samples were assigned age classifications of Modern, PreModern, or Mixed based on their ^3H activity in relation to the ^3H in the precipitation record (Michel and others, 2018) corrected for decay from the time of precipitation to the sample date. This age classification system is described in Lindsey and others (2019). Samples with ^3H less than 0.34 TU were categorized as PreModern because activities below this value would indicate that groundwater was recharged before 1950. Samples with ^3H greater than 2.6 TU were categorized as Modern because activities greater than this value would indicate that groundwater was recharged after 1950. Samples with activities between 0.34 and 2.6 were categorized as Mixed and indicate that groundwater was a mixture of water recharged before and after 1950.

Comparison of CE to UA model results showed that the CE model generally predicted higher recharge temperatures than the UA model for the same sample (fig. 27), but gave better fits and He balance ($\text{He}_{\text{terr}} = \text{He}_s - \text{He}_{\text{eq}} - \text{He}_a \approx 0$) for most of the Modern samples (23 of 40). The CE model may be more relevant to samples of Modern groundwater in this region because recharge is primarily from agricultural irrigation and can produce seasonal water-table fluctuations of around 1 m annually (Phillips and others, 2007; Jurgens and others, 2008). These fluctuations may trap large volumes of air in water that enters the aquifer as recharge. The UA model indicated that median excess air values were 2.6 cm^3/kg for Modern samples, 2.5 cm^3/kg for Mixed samples, and 1.41 cm^3/kg for PreModern samples, which indicates that Modern water has a larger amount of excess air than PreModern water.

Final dissolved gas models were chosen on a case-by-case basis by comparing model-fit parameters and statistics. Generally, samples with larger amounts of excess air or concentrations of gases indicative of F were fit better by the CE model than by the UA model (fig. 28). Final dissolved gas models are listed in the Final_ModOut worksheet in the example 4 workbook.

Chlorofluorocarbon and $^3\text{He}_{\text{trit}}$ concentrations were calculated from CFC and $\delta^3\text{He}$ samples and the dissolved gas models listed in the Final_ModOut worksheet. Tracer concentrations are computed in the Final_TrcOut worksheet and values with a red font are parameter errors taken from the Monte Carlo analysis. The R_{terr} value was determined from a best-fit line for samples with ^3H activities less than 0.29 TU, which is lower than the threshold used to define PreModern groundwater above, because it isolates the samples with the lowest ^3H concentrations. These samples had a R_{terr} value of about 5.0×10^{-7} , which indicates a mixture of radiogenic ($2 \times 10^{-8} \text{ cm}^3/\text{g}$) and mantle ($1 \times 10^{-5} \text{ cm}^3/\text{g}$) He (fig. 29). The amount of mantle He in the mixture is small, about 5 percent, and is probably derived from weathering of volcanic sediments in the aquifer (Page and Balding, 1973).

Tritogenic helium concentrations were calculated from the He mass balance (eqs. 23–25). Calculated $^3\text{He}_{\text{trit}}$ concentrations, for samples with He_{terr} concentrations of greater than 70 percent of the measured He concentration, are not reported because the amount of He_{terr} in such samples can make it difficult to accurately determine the amount of He derived from tritium decay. Samples that plot below the best-fit line shown on figure 29 will have negative or zero concentrations of $^3\text{He}_{\text{trit}}$ even though some of the samples have measurable ^3H . Those samples, and perhaps others, could be from sites where volcanic sediments are absent in the subsurface and have a purely radiogenic source of He_{terr} . For those sites, the R_{terr} values could be individually set to 2×10^{-8} on the _TrcOut worksheet, but the concentrations of $^3\text{He}_{\text{trit}}$ will be small. The best-fit R_{terr} value (5×10^{-7}) gives lower, more conservative estimates of $^3\text{He}_{\text{trit}}$ than a radiogenic R_{terr} , which may be preferable for a regional dataset. Figure 30 shows how the $\delta^3\text{He}$ graph can be manually adjusted to identify the $^3\text{He}_{\text{trit}}$ content of samples with mixtures of He_{terr} . For that graph, a concentration of 30 TU was set for the $^3\text{He}_{\text{trit}}$ value in the table to the right of the graph (fig. 30B). The graph shows that many samples with the He_{terr} plot near and along this mixing line, which indicates those samples have $^3\text{He}_{\text{trit}}$ values near 30 TU. Overall, 36 samples had calculated concentrations of $^3\text{He}_{\text{trit}}$ greater than 1 TU, 24 samples were not quantifiable, and 15 samples had calculated concentrations of less than 1 TU.

A

Dissolved Gas Modeling

1. Select samples to model 2. Select gases to model 3. Select parameters to model 4. Select models and options to model

Model all samples

Sample ID	Row Num
MER-05	4
MER-12	5
MER-20	6
MERFP-01	7
MERMW-05	8
MOD-06	9
MOD-10	10
TRLK-02	11
TRLK-10	12
TRLK-15	13
TRLKMW-01	14
CE-QPC-01	15
MER-02	16
MER-04	17
MER-09	18
MER-11	19
MER-16	20
MER-17	21
MER-19	22
MERMW-02	23
MERMW-03	24
MERMW-04	25

He, cm3/g
Ne, cm3/g
Ar, cm3/g
Kr, cm3/g
Xe, cm3/g
N2, cm3/g
Ar, mg/L
N2, mg/L
O2, mg/L
CO2, mg/L
CH4, mg/L
H2, mg/L
N2O, mg/L

Parameters

Temperature
 Excess air
 Salinity
 Elevation / pressure
 Fractionation (excess air)
 Excess nitrogen gas

Models

Unfractionated excess air (UA)
 Partial re-equilibration (PR)
 Closed-system equilibration (CE)

Model options

Use alt. search method
 Rerun bad fits with reduced gases
 Calculate excess nitrogen gas
 Run Monte Carlo simulations
 Excess N2 for Ar/N2 only

5. RUN MODELS CLOSE FORM

B

Dissolved Gas Modeling

1. Select samples to model 2. Select gases to model 3. Select parameters to model 4. Select models and options to model

Model all samples

Sample ID	Row Num
MER-05	4
MER-12	5
MER-20	6
MERFP-01	7
MERMW-05	8
MOD-06	9
MOD-10	10
TRLK-02	11
TRLK-10	12
TRLK-15	13
TRLKMW-01	14
CE-QPC-01	15
MER-02	16
MER-04	17
MER-09	18
MER-11	19
MER-16	20
MER-17	21
MER-19	22
MERMW-02	23
MERMW-03	24
MERMW-04	25

He, cm3/g
Ne, cm3/g
Ar, cm3/g
Kr, cm3/g
Xe, cm3/g
N2, cm3/g
Ar, mg/L
N2, mg/L
O2, mg/L
CO2, mg/L
CH4, mg/L
H2, mg/L
N2O, mg/L

Parameters

Temperature
 Excess air
 Salinity
 Elevation / pressure
 Fractionation (excess air)
 Excess nitrogen gas

Models

Unfractionated excess air (UA)
 Partial re-equilibration (PR)
 Closed-system equilibration (CE)

Model options

Use alt. search method
 Rerun bad fits with reduced gases
 Calculate excess nitrogen gas
 Run Monte Carlo simulations
5000 Write MC sims to file
 Assume gases are independent
 Excess N2 for Ar/N2 only

5. RUN MODELS CLOSE FORM

Figure 26. The Dissolved Gas Modeling form used to generate *A*, unfractionated excess air models (UA) and *B*, closed-system equilibration models (CE) of dissolved gases on the basis of dissolved neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe) concentrations in groundwater in the central eastside of the San Joaquin Valley, California, in 2006.

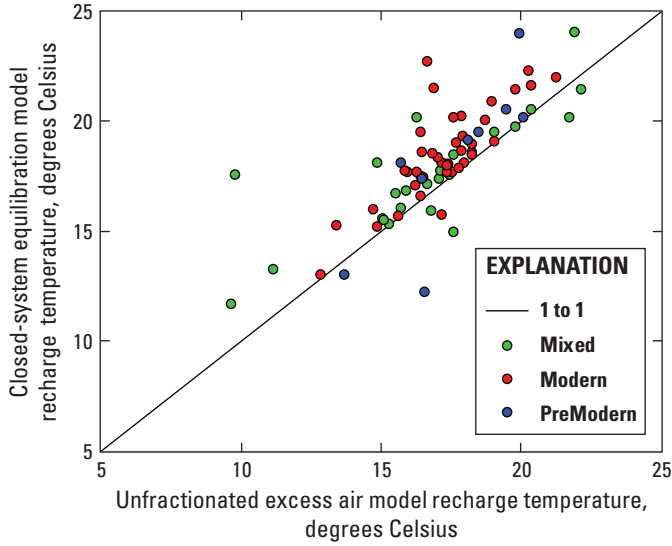


Figure 27. Comparison of closed-system equilibration and unfractionated excess air model results for recharge temperatures among different age classifications based on tritium measurements of groundwater samples from the central eastside of the San Joaquin Valley, California, in 2006.

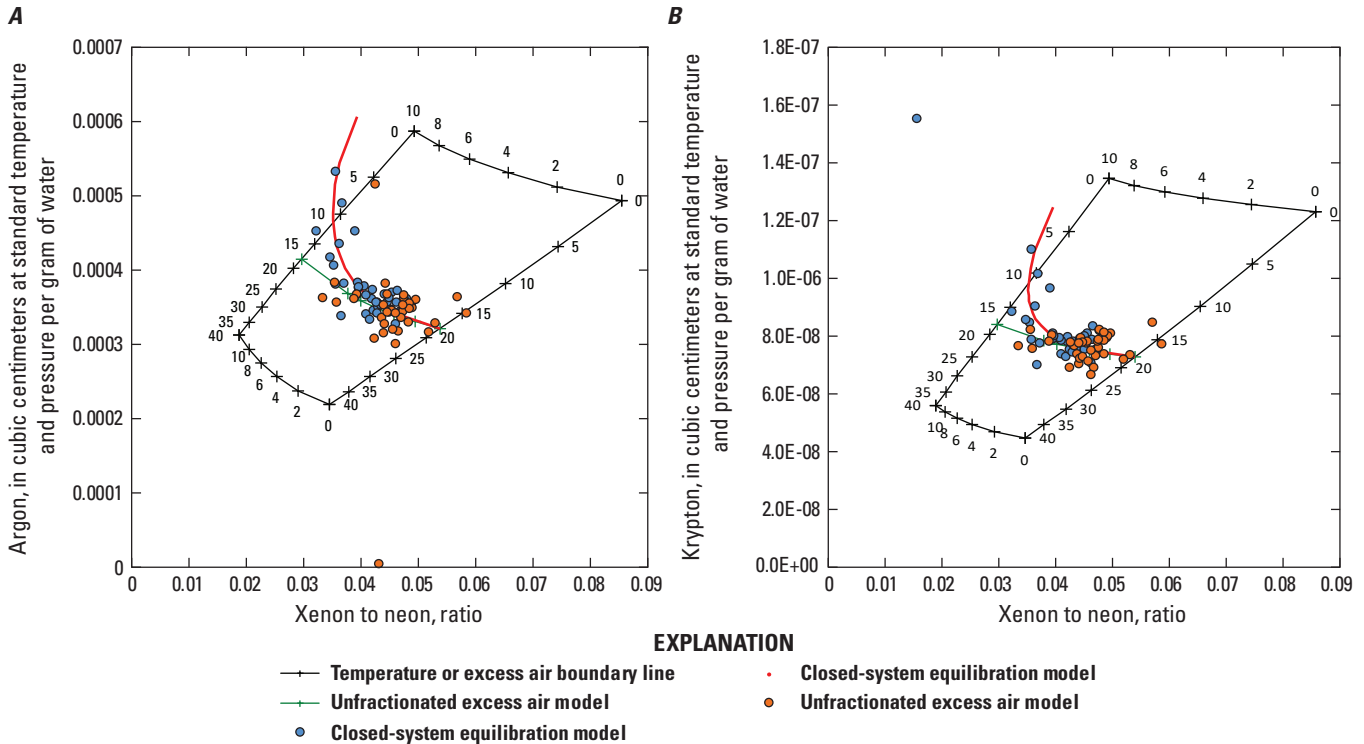
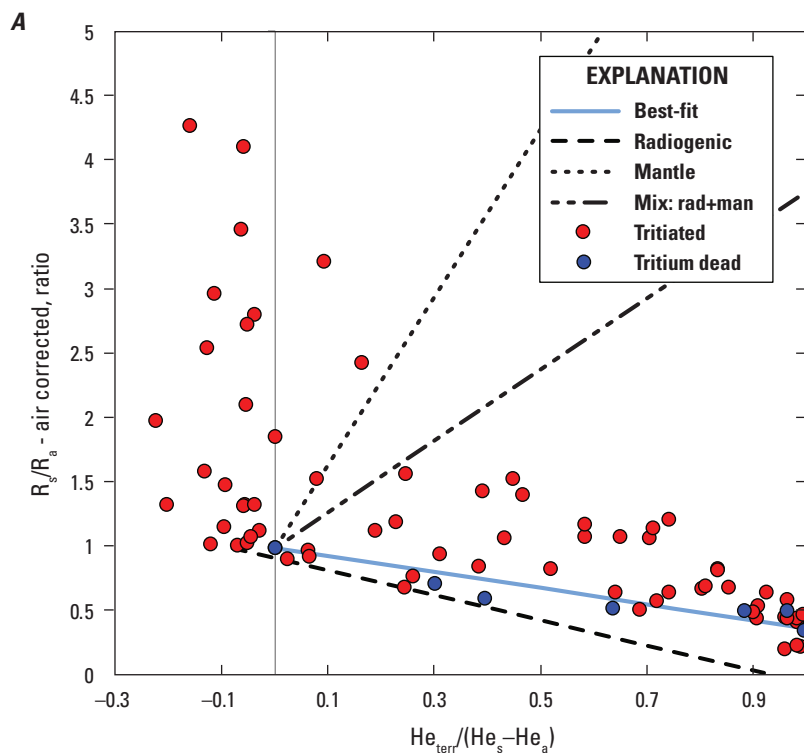


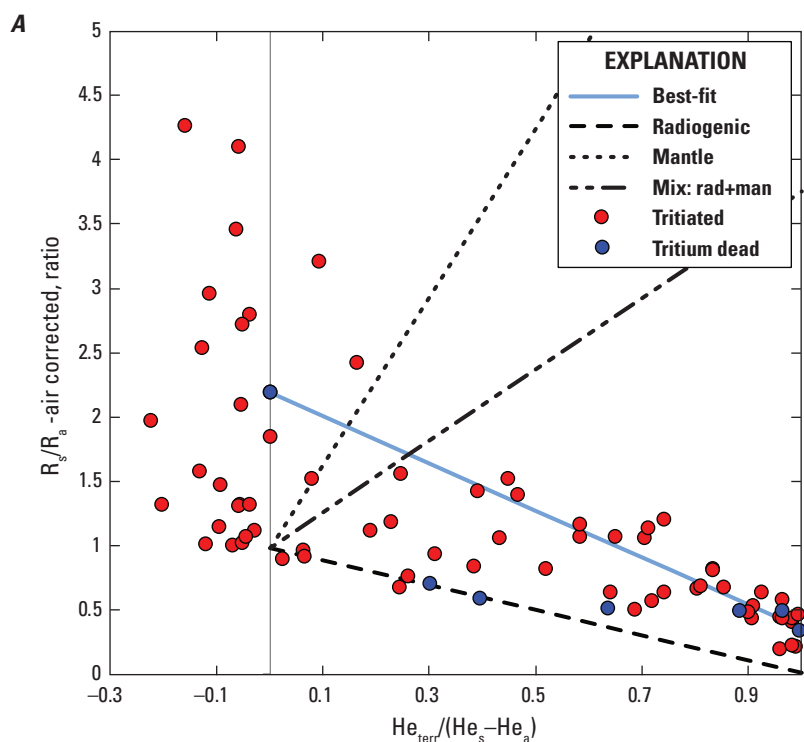
Figure 28. Graphs of sample concentrations of *A*, argon versus xenon to neon and *B*, krypton versus xenon to neon. Samples are color coded based on the final dissolved gas model for each sample. Samples where the unfractionated excess air (UA) model was used are orange and samples where the closed-system equilibration (CE) model was used are blue. Most samples that follow a UA model (orange circles) had excess air values between 1 and 4 cubic centimeters per kilogram (cm^3/kg). Many samples also followed a CE model with excess air values between 3 and 7 cm^3/kg . The lines for the UA (green-solid line) and CE (red-dotted line) were plotted using a temperature of 17 degrees Celsius and the fractionation parameter of the CE model was set to 0.5.



B

	CA	CB	CC	CD	CE	CF	CG
							Mixture of radiogenic and mantle
Mantle helium, %			na	na	na	50%	
Rterr			4.95E-07	2E-08	1.04E-05	5.2E-06	
Rterr/Ra			0.357408	0.014451	7.5	3.757225	
He-3 (trit)			0	0	0	0	
He(terr) / (He(s) - He(a))							
		R/Ra	R/Ra	R/Ra	R/Ra		=Req
0		0.983	0.983	0.983	0.983		
0.25		0.826602	0.740863	2.61225	1.676556		
0.5		0.670204	0.498725	4.2415	2.370113		
0.75		0.513806	0.256588	5.87075	3.063669		
1		0.357408	0.014451	7.5	3.757225		=Rterr

Figure 29. Views of *A*, the modified Weise plot (Weise and Moser, 1987) for samples that are tritiated (tritium concentration greater than 0.29 tritium unit; TU) and samples that are tritium-dead (less than 0.29 TU) and *B*, a table of helium isotope control variables on the Final_TrCOut worksheet. The best-fit line (solid blue) through tritium-dead samples has a helium-3/helium-4 of terrigenous helium (R_{terr}) of about 5.0×10^{-7} and indicates a mixture of radiogenic and mantle helium.



B

	CA	CB	CC	CD	CE	CF	CG
							Mixture of radiogenic and mantle
Mantle helium, %			na	na	na	50%	
Rterr			4.95E-07	2E-08	1.04E-05	5.2E-06	
Rterr/Ra			0.357408	0.014451	7.5	3.757225	
He-3 (trit)			30	0	0	0	
He(terr) / (He(s) - He(a))							
		R/Ra	R/Ra	R/Ra	R/Ra		=Req
0		2.188655	0.983	0.983	0.983		
0.25		1.730843	0.740863	2.61225	1.676556		
0.5		1.273032	0.498725	4.2415	2.370113		
0.75		0.81522	0.256588	5.87075	3.063669		
1		0.357408	0.014451	7.5	3.757225		=Rterr

Figure 30. Views of *A*, the modified Weise plot showing mixing of groundwater endmembers and *B*, a table of helium isotope control variables on the Final_TrCOut worksheet. The blue line illustrates a mixture of water from one source that has no terrigenous helium (He_{terr}) and 30 tritium units (TU) of tritogenic helium-3 ($^3He_{trit}$), and another water with 0 TU of $^3He_{trit}$ and is almost entirely composed of terrigenous helium that has a helium-3/helium-4 ratio (R_{terr}) of 5.0×10^{-7} .

Finally, the example workbook that accompanies DGMETA (DGMETA_Example_4.xlsm) has an additional _ModOut worksheet with results from the samples where the CE model was used. These results have Monte Carlo simulations that were computed assuming the gases are completely independent. These results can be compared to the Final_ModOut version that included Monte Carlo simulations that were done assuming that the gases were not independent and were randomized as a group. The gas samples generated, assuming complete independence, are truly random and provide a more accurate picture about the true range of possible solutions to the measured gas data. Thus, the parameter error estimates from this method can often be large when the range of possible solutions is large. In addition, the average results of the ensemble may not be similar to the best-fit results computed from the measured gas data. In this example, the temperature, entrapped air, and F results from the Monte Carlo results deviate from the best-fit results by about -2.6, -87, and 9.2 percent, respectively. Overall, the completely independent results produced warmer temperatures with larger amounts of entrapped air than indicated by the fit computed from the measured data. These results also could be used to compute tracer concentrations, but the atmospheric mole fractions have errors as large as the computed mole fraction, which makes the tracer results ineffective for determining ages of water.

In contrast to the completely independent set of Monte Carlo simulations, the gas samples generated as a randomized group provided a more local estimate of the range of possible solutions and, therefore, had smaller parameter errors. In addition, the Monte Carlo simulations more strongly agreed with best-fit results computed from the measured data. Here, the temperature, entrapped air, and F values of the Monte Carlo simulations deviate from the best-fit parameter estimates by about 0.3, -4.7, and 0.17 percent, respectively. The dependent set of Monte Carlo errors also give lower computed errors associated with tracer concentrations. Consequently, this approach to parameter uncertainty can provide a reasonable substitute for the large uncertainty surrounding some CE model results.

Although this approach for dealing with large parameter uncertainties is advantageous for reporting CE model results and for computing tracer concentrations from those models, it may sidestep a more detailed analysis of Monte Carlo results recommended by Jung and Aeschbach-Hertig (2018). But more importantly, it also may mask important yet unexplained physical controls that might better explain peculiar sets of noble gas data. A more detailed analysis of the noble gas data in the context of new or existing physical processes and mixing of water with different recharge histories in the subsurface could therefore reveal a better model of the noble gas data.

Example 5—Degassed Groundwater

Aeschbach-Hertig and others (2008) showed that the CE model can explain some situations in which gases exsolve from a solution into a gas or bubble phase. Degassing can cause the gases to fractionate according to their solubility such that the lighter noble gases with lower solubilities are preferentially depleted from the solution relative to the heavier noble gases. The CE model simulates this behavior when F is greater than 1, which physically can be interpreted as the creation of bubbles from the water in response to a drop in hydraulic pressure. Bubble creation may occur as groundwater is extracted from deeper depths or moves to an area of lower pressure or warmer temperature. This phenomenon also can occur in groundwater where oversaturation of N₂ from denitrification or CH₄ from methanogenesis cause other gases to exsolve from a solution or to be undersaturated in the subsurface (Aeschbach-Hertig and others, 2008; Cey and others, 2009). In the mathematical formulation of the CE model, the F parameter includes the ratio of the final volume of entrapped gas to the initial volume of entrapped gas. When F is greater than 1, the final volume of entrapped gas is greater than the initial volume indicating the enlargement or creation of a trapped volume of gas.

DGMETA can be used to graphically identify cases in which degassing likely occurred and estimate dissolved gas model parameters in which the CE model describes degassing in samples. A convenient way to identify degassed samples is to make graphs of the Xe/Ne ratio because degassing tends to cause Ne (a lighter gas) to be depleted relative to Xe (a heavier gas) and leads to higher Xe/Ne ratios in comparison to samples that are not degassed. Figure 31 shows samples from Aeschbach-Hertig and others (2008) in relation to the CE model with a F parameter value set to 2 and a recharge temperature set to 9 °C on the _GasGph worksheet. The samples plot far to the right of normal samples with dissolved excess air concentrations and higher Xe/Ne ratios.

In order to numerically solve for the best-fit parameters of degassed samples, the initial value of the F parameter should be set to a value of greater than 1 on the Input_Gases worksheet because the excess air component of the CE model vanishes at F=1. For this reason, it is recommended that degassed samples first be identified through graphical inspection of gas-gas graphs. Setting the initial F factor to a value greater than 1 ensures the numerical solution will identify the proper best-fit values of degassed samples. For the degassed samples of Aeschbach-Hertig and others (2008), the initial F value was set to 1.5 and best-fit solutions were computed. Results computed using DGMETA were nearly the same as best-fit values reported by Aeschbach-Hertig and others (2008).

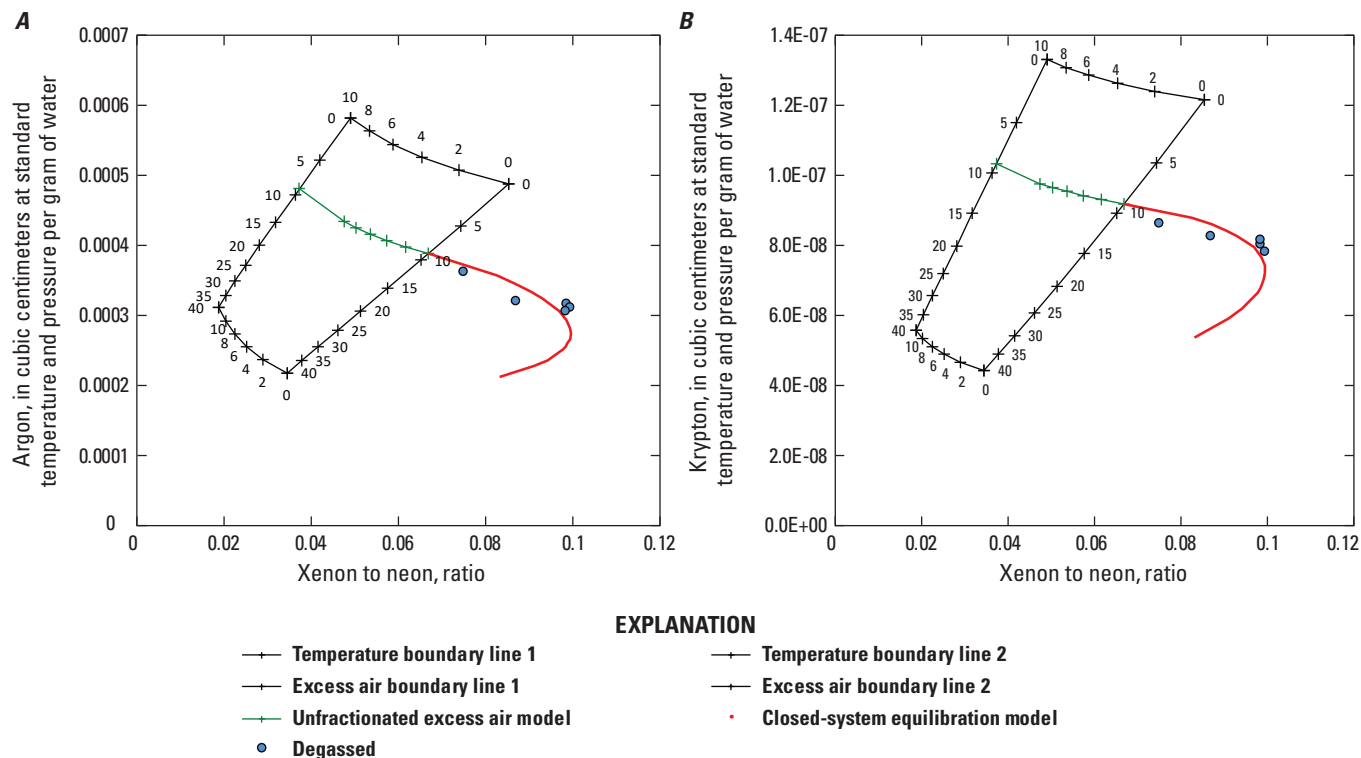


Figure 31. Solubility concentrations for A, argon and B, krypton plotted versus the ratio of the solubility concentrations of xenon and neon, in cubic centimeters per gram of water (cm^3/g), for different recharge temperatures and excess air values. Degassed samples from Aeschbach-Hertig and others (2008) are plotted to show the area where degassed samples can be identified. Dissolved gas model output for the unfractionated excess air model is shown by the green line and the closed-system equilibration (CE) model is the red-dotted line. The samples are consistent with the CE dissolved gas model with a recharge temperature of 9 degrees Celsius and a fractionation value of about 2. The salinity and elevation of the degassed samples were approximately 1.3 per mil and 88 meters ($\text{pressure} = 0.99 \text{ atm}$), respectively. The red dots give CE dissolved gas model concentrations and ratios for different amounts of entrapped excess air.

Installation Notes

The program was written in Visual Basic for Applications within the Microsoft Excel environment. As such, the program requires Excel macros to be enabled in order to work. An Excel warning may appear in the toolbar when the program is first opened, indicating that macros have been detected and are disabled. Users must enable Excel macros for the program to work.

Disclaimer

This software has been approved for release by the U.S. Geological Survey (USGS). Although the software has been subjected to rigorous review, the USGS reserves the right to update the software as needed pursuant to further analysis and review. No warranty, expressed or implied, is made by the USGS or the U.S. Government as to the functionality of the software and related material nor shall the fact of release constitute any such warranty. Furthermore, the software is released on condition that neither the USGS nor the U.S. Government shall be held liable for any damages resulting from its authorized or unauthorized use.

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For additional information, contact

NAWQA Science Team

U.S. Geological Survey

12201 Sunrise Valley Drive, MS 413

Reston, VA 20192-0002

Email: gs-w_opp_nawqa_science_team@usgs.gov

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