Calculation of dissolved gas concentrations and isotope ratios from measurements made after static headspace extraction

Dissolved gases are commonly extracted into a gaseous headspace using a static headspace equilibration technique (Ioffe and Vitenberg 1984) so that the headspace can be analyzed by gas chromatography or mass spectrometry. Here I describe how I calculate the dissolved gas concentrations originally present in the sample water from the final headspace gas concentrations, and how to correct for equilibrium isotopic fractionation in the case of isotopic measurements on the headspace gas. Formulas for these calculations are given in an Excel spreadsheet entitled "Dissolved gas headspace equilibration.xls".

Prediction of dissolved gas concentrations in water at atmospheric equilibrium

The first worksheet ("Air equil H$_2$O") predicts the dissolved gas concentrations in water that has equilibrated with air at a particular temperature and elevation. This is useful because some of these gases (e.g., N$_2$, Ar) are usually close to atmospheric equilibrium in environments such as streams, and because air-equilibrated water can be analyzed as an approximate standard. Natural waters exchange gases with overlying air that is likely to be water-saturated, so the partial pressures for dry air are corrected for saturation vapor pressure, which if not measured directly can be estimated from temperature using an empirical function given in Benson and Krause (1980).

The equilibrium concentration (Liters gas per Liter of solution) of a particular gas dissolved in the liquid phase (C$_{liq}$) is related to its partial pressure in the gas phase (P$_{gas}$ in atm) by the Bunsen solubility coefficient:

$$C_{liq} = P_{gas} \cdot \beta_T \cdot P_{BAROMETRIC}$$

where β_T is the solubility coefficient in units of L L^{-1} atm^{-1}, calculated for the temperature at which the air-water equilibration took place (see below). The barometric pressure (in atm) corrects for the reduced total pressure at altitude, and/or short-term variations in barometric pressure that can be measured during sampling.

The Bunsen solubility coefficient (β_T) is estimated from temperature in kelvins using polynomial equations for zero salinity derived from the references in the following table. Alternatively, similar equations can be employed to estimate a solubility coefficient (K$_T$) in units of mol gas (L gas)$^{-1}$ atm^{-1}. Published empirical equations are usually for one or the other of these units. For gases that are nearly ideal in their behavior, these two alternative solubility coefficients can be interconverted approximately by this relation:

$$K_T = \beta_T/V = \beta_T/RT$$

Where V is the volume of one mole of pure gas at STP (= RT using the Ideal Gas Law, with T = 273.15 K), and the aqueous solution is assumed to approximate the density of freshwater. I prefer to use the original published empirical equations, so I can check the results against tabulated data in the papers, and then when necessary convert the concentration units between L gas/L solution and moles gas/L solution using the Ideal Gas Law:

moles gas/L solution = (L gas/L solution)/RT = (L gas/L solution)/(0.0821*273.15)

The polynomial equations are generally of the following form, with constants denoted by *A* and *T* representing the equilibration temperature in kelvins (°C + 273.15):

$$\ln(\beta_T) = A_1 + A_2(100/T) + A_3\ln(T/100)$$

Gas	References for gas solubility coefficients
CH_4	Yamamoto, S., J.B. Alcauskas, and T.E. Crozier. 1976. Solubility of methane in distilled water and seawater. J. Chem. Eng. Data 21: 78-80.
N_2, O_2, Ar	Weiss, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. Deep-Sea Res. 17: 721-735.
CO_2	Weiss, R.F. 1974. Carbon dioxide in water and seawater: The solubility of a non-ideal gas. Mar. Chem. 2: 203-215.
O_2	Benson, B.B. and D. Krause, Jr. 1984. The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere. 1. Oxygen. Limnol. Oceanogr. 25: 662-671.
N_2O	Weiss, R.F. and B.A. Price. 1980. Nitrous oxide solubility in water and seawater. Mar. Chem. 8: 347-359

In addition to predicting dissolved gas concentrations in air-equilibrated water, this worksheet also predicts the results of a static headspace equilibration using a sample of this water. This calculation is based on the following mass-balance equation, in which concentration units can be μM and volume units can be L:

$$(C^0_{liq})(V_{liq}) = (C_{liq})(V_{liq}) + (C_{gas})(V_{gas})$$

where C^0_{liq} is the original gas concentration and C_{liq} and C_{gas} are the concentrations in the liquid and gas phases after equilibration. Assuming equilibrium inside the vessel, we can substitute C_{liq} with $P_{gas} \cdot \beta_T \cdot P_{BAROMETRIC}$ as discussed above, and rearrangement of this equation to solve for the headspace gas concentration C_{gas} yields:

$$(C_{gas}) = (C^0_{liq} \cdot V_{liq})/[(\beta_T \cdot P_{BAROMETRIC} \cdot V_{liq}) + V_{gas}]$$

This gas concentration in μmoles/L can be converted to units of ppmv using the Ideal Gas Law:

$$ppmv = (\mu moles/L)(RT)$$

where R is the gas constant which is 0.0821 L·atm mole^{-1} °K^{-1}, and T is 273.15 °K.

Finally, the total μmoles of gas in the headspace can be calculated as $C_{gas} \cdot V_{gas}$ and that provides an estimate of sample size (with appropriate correction for any subsampling of the headspace). This information can be used to predict how much gas gets into the sample vial after accounting for any subsampling of the headspace, as is done for the case of LINX 2 in the present protocols.

Calculation of original dissolved gas concentrations

The second worksheet ("Sample analysis") is set up for the analysis of unknown samples by static headspace equilibration in a closed vessel, followed by measurement of gases in the headspace. Calculation of the original gas concentrations in the sample water is based on the concentrations measured in the headspace, the solubility coefficients (see above), and the mass balance for the gas-liquid system. Example data are provided that represent the air-equilibrated water examples in the other worksheet.

Gases in the headspace are often measured as partial pressures in atm (~ L gas/L volume) and are here converted to μmoles gas/L for the calculations using the Ideal Gas Law (PV = nRT):

$$C_{gas} = n/V = (P/RT) * (10^6 \ \mu moles/mole)$$

Where V is 1 L, P is the measured partial pressure in atm, R is the constant 0.0821 L·atm mole^{-1} °K^{-1}, and T is the STP temperature in kelvins (273.15).

Oxygen and argon are often measured together as a single peak by gas chromatography, so the spreadsheet is designed to accommodate that. Argon is subsequently estimated from the expected molar ratio of N_2 to Ar in the headspace (38.6 at 25°C) and O_2 is assumed to comprise the remainder of the measured partial pressure.

After calculating the final equilibrium gas concentrations in the liquid phase (C_{liq}; see above), the following mass-balance equation, in which concentration units are µM and volume units are L, allows calculation of the total µmoles of gas in the vessel

$$\text{Total µmoles of gas} = (C_{liq})(V_{liq}) + (C_{gas})(V_{gas})$$

The mass-balance equation presented earlier allows calculation of the original gas concentration, C^0_{liq}, in units of µM, but here it is modified to account for cases where the source headspace gas is impure:

$$(C^0_{liq})(V^0_{liq}) = (C_{liq})(V_{liq}) + (C_{gas})(V_{gas}) - (C_{sourcegas})(V_{gas})$$

Solving for C^0_{liq} therefore yields:

$$(C^0_{liq}) = [(C_{liq})(V_{liq}) + (C_{gas})(V_{gas}) - (C_{sourcegas})(V_{gas})]/(V^0_{liq})$$
$$= [(\text{total µmoles of gas}) - (C_{sourcegas})(V_{gas})]/(V^0_{liq})$$

Correcting for isotopic equilibrium fractionation (not in the spreadsheet but was considered for LINX2 calculations and deemed unnecessary)

Headspace gas measurements are affected by the equilibrium isotopic fractionation between the gas and liquid phases. This fractionation makes little difference for the more insoluble gases and for highly ^{15}N-enriched samples, but may need to be accounted for when samples approach natural abundance, and is most important for the relatively soluble gases such as N_2O and CO_2, as shown in this comparison of N_2 and N_2O under several scenarios of varying headspace and liquid volumes:

	Headspace volume (mL)	Water volume (mL)	% gas in headspace
N_2	30	30	98.6
N_2	15	45	95.8
N_2	5	8	97.7
N_2O	30	30	65.2
N_2O	15	45	38.5
N_2O	5	8	54.0

The equilibrium isotope fractionation factor is commonly denoted as α and is herein defined as follows for the case of N_2 or N_2O gas dissolving in water:

$$\alpha = {}^{15}N:{}^{14}N_{(GAS\ PHASE)} / {}^{15}N:{}^{14}N_{(DISSOLVED\ GAS)}$$

The fractionation can also be expressed as an enrichment ε, defined as α minus 1, which when multiplied by 1000 gives units of per mil (‰).

A check of the literature revealed that α values for N_2 and N_2O do not vary over the range of streamwater temperatures we will encounter, and the best available estimates appear to be the following:

N_2 α = 0.99915 (ε = -0.85 ‰) from Benson and Parker (1961), Klots and Benson (1963)

N_2O α = 0.99925 (ε = -0.75 ‰) from Inoue and Mook (1994)

Thus at equilibrium between the headspace and liquid, the dissolved N_2 and N_2O will be enriched by 0.85 and 0.75 ‰, respectively, compared to the overlying gas phase.

For our purposes, we need to correct our $\delta^{15}N$ measurement of the headspace gas for any tracer ^{15}N that remains in solution after the equilibration. This can be accomplished with the following isotopic mass-balance equation:

$$[\delta^{15}N_{(ORIGINAL\ SAMPLE)} * M_{(ORIGINAL\ SAMPLE)}] =$$
$$[\delta^{15}N_{(HEADSPACE)} * M_{(HEADSPACE)}] + [\delta^{15}N_{(LIQUID)} * M_{(LIQUID)}]$$

where M is mass (e.g., in μmoles as in my spreadsheet), $M_{(HEADSPACE)}$ is corrected for any subsampling if necessary, and:

$$\delta^{15}N_{(LIQUID)} = \delta^{15}N_{(HEADSPACE)} - \varepsilon$$

This calculated $\delta^{15}N_{(ORIGINAL\ SAMPLE)}$ can then be corrected for background $\delta^{15}N$ measurements that were made and corrected in the same fashion.

For example, suppose that you sample a stream for N_2O, and that streamwater had equilibrated with the atmosphere at 25 deg C to produce a dissolved N_2O concentration of 0.007304 μM. The headspace equilibration was performed at 25 deg C. The water and gas volumes for the equilibration were 0.041 and 0.019 L, respectively. The $M_{(ORIGINAL\ SAMPLE)}$ in the 0.041-L sample was 0.000299 μmoles of N_2O. If the final $\delta^{15}N_{(HEADSPACE)}$ had been measured at +10 ‰, then applying the above mass balance shows that the $\delta^{15}N_{(ORIGINAL\ SAMPLE)}$ was +10.42 ‰. Similarly, if for N_2O the final $\delta^{15}N_{(HEADSPACE)}$ had been measured at +100.0 ‰, the $\delta^{15}N_{(ORIGINAL\ SAMPLE)}$ would have been +100.54 ‰. The same calculation for the less soluble gas N_2, if the headspace were measured to be +10 ‰, yields a corrected $\delta^{15}N$ of 10.07 ‰! These corrections become significant only at low levels of enrichment, and only for relatively soluble gases.

References
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