

Calculations

Note: for this help document, we use `mutate()` often to add all these terms to the dataframe. This is just as a sample calculation so you can see all the steps. In the final function, this is all done ‘under the hood’ and it will only output the final calculated values of $p\text{CO}_2$.

Introduction

Here we go through all the calculations, assumptions, and constants to calculate $p\text{CO}_2$ values that takes into account salinity (due to preservation of samples).

Values are calculated using the headspace equilibrium technique (ref goes here). Briefly, a sample of water is taken, preserved in-field, and brought back to the lab for analysis. In the lab, water is removed from the container at-the-same-time as helium is injected in its place. The sample is then gently shaken to allow CO_2 to equilibrate between the liquid and gas phase. A gas sample is then taken and injected into a gas chromatograph, where we get CO_2 values (in ppm).

Up to this point, a number of parameters are already known. They include:

- Water temperature in field (C)
- Air pressure in field (kPa)
- Water temperature in lab during analysis (C)
- Air pressure in lab during analysis (kPa)
- Salt added (for preservation of samples; g)
- Weight of the sampling container (g; empty)
- Weight of full container(g; water and container)
- Weight of the container with headspace (g)
- Injected amount of helium (mL) - CO_2 value from GC (ppm)

You would begin by creating a dataframe `dat` such as:

```
## -- Attaching packages ----- tidyverse 1.3.0 --

## v ggplot2 3.3.2      v purrr   0.3.4
## v tibble  3.0.4      v dplyr   1.0.2
## v tidyr   1.1.2      v stringr 1.4.0
## v readr   1.4.0      v forcats 0.5.0

## -- Conflicts ----- tidyverse_conflicts() --
## x dplyr::filter() masks stats::filter()
## x dplyr::lag()    masks stats::lag()
```

Conversions

The first thing we do is convert the input values to the units used in the various calculations, as well as calculate the total water volume before and after headspace:

```
dat <- dat %>%
  mutate(temp_field_K = temp_field_C + 273.15,
         temp_lab_K = temp_lab_C + 273.15,
         p_field_atm = p_field_kPa * 0.009869,
         p_lab_atm = p_lab_kPa * 0.009869,
         vol_water_L = (exe_full_g - exe_g)/1000, #assuming density of 1.00 (g~mL))
```

```
vol_HS_L = (exe_full_g - exe_headspace_g)/1000,
vol_waterHS_L = (vol_water_L - vol_HS_L),
he_inj_L = he_inj_mL/1000)
```

Calculate the moles of $p\text{CO}_2$ in vial

The headspace-equilibria method results in the partitioning of CO_2 between the water in the vial and the helium (He) headspace. When we measure the gas in the vial, we get the CO_2 in ppm, and is equivalent to x (ppm volume):

$$p\text{CO}_2 = x \times P_{\text{air}}$$

Brief review of gas units ppmv is equivalent to 1 gas volume per 10^6 air volumes or 1 uL per 1L of air

We can use this equation with the Ideal Gas Law to get the moles of CO_2 in the headspace. But what is P_{air} after we've injected He?

Calculation of new P in headspace after He injection

We know mass is conserved during equilibration between the water and gas, but we also assume the exsolution of other gases does not affect the headspace pressure (i.e. H_2O , N_2O , N_2 , O_2 , Ar).

Thus, for He we get:

$$\text{mol}_{\text{aq}} + \text{mol}_{\text{g}} = \text{mol}_{\text{total}}$$

where mol_{aq} = concentration of He
 mol_{g} = ideal gas of He in headspace
 $\text{mol}_{\text{total}}$ = ideal gas injected

We can substitute in what we know:

$$V_{\text{sampleHS}} \times (K_H \times P_{\text{He}})] + \frac{P_{\text{He}} \times V_{\text{HS}}}{R \times T} = \frac{P_{\text{lab}} \times V_{\text{inj}}}{R \times T}$$

Re-arrange and solve for the unknown P_{He} :

$$P_{\text{He}} = \frac{\left(\frac{P_{\text{lab}} \times V_{\text{inj}}}{R \times T}\right)}{V_{\text{sampleHS}} \times K_H + \frac{V_{\text{HS}}}{R \times T}}$$

This gives us the new P in the headspace (P_{He}), which we need to calculate the dissolved CO_2 .

First, we need to calculate the K_H for helium at our analytical pressure (assuming He behaves like an ideal gas) using the van't Hoff equation:

$$K_H = K_{H\text{std}} \times \exp\left(\frac{\Delta H}{R} \times \left(\frac{1}{T} - \frac{1}{T_{\text{std}}}\right)\right)$$

```
#calculate Kh of He at the lab temperature
dat <- dat %>%
  mutate(Kh_he = 0.00038 * exp(92 * ((1/temp_lab_K) - (1/298.15)))) )
```

Then we can calculate the pressure in the headspace (P_{He}):

```
#define the gas constant (R; L atm / mol K)
R_gas <- 0.08205737

dat <- dat %>%
  mutate(p_He_atm = ((p_lab_atm * he_inj_L)/(R_gas * temp_lab_K)) / ((vol_waterHS_L * Kh_he) + (vol_HS_L
```

Back to it...

Ok, so going back to our original equation of $pCO_2 = x \times P_{air}$, but in this case, P_{air} is actually P_{He} we just calculated!

Thus, we get:

$$pCO_2 = \frac{x}{10^6} \times P_{He}$$

which gives us our pCO_2 in the headspace of our vial.

```
#calculate pCO2 in headspace
dat <- dat %>%
  mutate(pCO2_HS = (measCO2_ppm / (10^6)) * p_He_atm )
```

Now we can use Henry's Law to calculate the dissolved concentration of CO_2 in the water of the vial with headspace.

Calculation of dissolved CO_2 using Henry's Law

Henry's Law states:

$$K_{CO_2} = \frac{[CO_2]}{pCO_2}$$

and we can re-arrange it to get the dissolved CO_2 :

$$[CO_2] = K_{CO_2} \times pCO_2$$

at the lab pressure and temperature!

However, we need to correct the Henry constant for pCO_2 (K_{CO_2}) for lab temperature and salinity.

Temperature and Salinity Correction for K_{CO_2}

We use the temperature and salinity corrected equations to determine CO_2 solubility based on Weiss 1974. This equation is a combination of the van't Hoff and Setchenow equations.

To calculate the temperature and salinity corrected K_H for CO_2 (in $\text{mol L}^{-1}\text{atm}^{-1}$), we use:

$$\ln K_0 = A_1 + A_2(100/T) + A_3 \ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2]$$

where

T = sample temperature (in K)

S = salinity (‰)

and the rest are constants from Weiss (1974):

$A_1 = -58.0931$

$A_2 = 90.5069$
 $A_3 = 22.294$
 $B_1 = 0.027766$
 $B_2 = -0.025888$
 $B_3 = 0.0050578$

Now we calculate K_H corrected for temperature and S:

```

#define constants
a1 <- -58.0931
a2 <- 90.5069
a3 <- 22.294
b1 <- 0.027766
b2 <- -0.025888
b3 <- 0.0050578

#calculate salinity
dat <- dat %>%
  mutate(sal_permil = KCl_added_g / vol_water_L)

#calculate Kh of CO2 (mol/L atm)
#remember, 'log' here is 'ln' (not log10())
dat <- dat %>%
  mutate(Kh_co2 = exp(a1 + (a2*(100/temp_lab_K)) + (a3 * log(temp_lab_K/100)) + (sal_permil * (b1 + (b2

```

Back to it...

and from that calculate the concentration of dissolved CO₂ in the vial with headspace:

```

#calculate CO2 concentration in vial water (with headspace)
dat <- dat %>%
  mutate(CO2_vial_mol.L = Kh_co2 * pCO2_HS)

```

Calculate the [CO₂] in the original vial

We have the concentration of CO₂ in both the water with headspace, and in the headspace itself. Now we want to calculate the CO₂ concentration in the vial *before* we created a headspace.

To do this, we assume all CO₂ was dissolved, thus:

$$\frac{n_{\text{HS}} + n_{\text{dissolved}}}{V_{\text{sample+HS}}} = [\text{CO}_2]$$

where

$V_{\text{sample+HS}}$ = volume of the vial with sample and headspace

$$\frac{\frac{p\text{CO}_2 \times V_{\text{HS}}}{R \times T} + ([\text{CO}_2]_{\text{diss}} \times V_{\text{sample+HS}})}{V_{\text{sample+HS}}} = [\text{CO}_2]_{\text{orig}}$$

where

$[\text{CO}_2]_{\text{orig}}$ represents the concentration of CO₂ in the vial with no headspace (i.e. vial as it came from the field), and represents the concentration of CO₂ in the water at time of sampling.

```
#calculate the [CO2] in water (before headspace)
dat <- dat %>%
  mutate(n_HS = (pCO2_HS * vol_HS_L)/(R_gas * temp_lab_K),
         n_diss = CO2_vial_mol.L * vol_waterHS_L,
         co2_orig = (n_HS + n_diss) / vol_waterHS_L)
```

Calculate the various units of pCO₂ (uM, atm, and %-saturation)

We can calculate the CO₂ %-saturation with respect to the atmosphere via:

$$\text{Percent-saturation} = \frac{[\text{CO}_2]_{\text{orig}}}{[\text{CO}_2]_{\text{sat}}} \times 100$$

Which can be calculated as:

$$\text{Percent-saturation} = \frac{[\text{CO}_2]_{\text{orig}}}{K_H \times (\text{CO}_2_{\text{atm}} \times 10^{-6} \times P_{\text{field}})} \times 100$$

where

K_H is calculated at the field temperature and pressure

CO_{2 atm} is the atmospheric concentration of CO₂

```
#set the atmospheric concentration of CO2
CO2_air_ppm <- 410

#calculate Kh of CO2 for the field (only the first half of Weiss 1974)
dat <- dat %>%
  mutate(Kh_co2_field = exp(a1 + (a2*(100/temp_field_K)) + (a3 * log(temp_field_K/100))),
         CO2_perc_sat = (co2_orig / (Kh_co2_field * (CO2_air_ppm * (10^-6) * p_field_atm))) * 100)
```

Finally, we end with calculating the various pCO₂ units

```
dat <- dat %>%
  mutate(pCO2_uM = co2_orig * 10^6,
         pCO2_uatm = (co2_orig / Kh_co2_field) * 10^6)
```