

Temperature Dependence of pCO₂

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September 2, 20120

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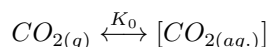
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Introduction

It turns out pCO₂ is not a simple measure of the concentration (or activity) of CO₂ in water, as it is strongly influenced by temperature. Even at a fixed concentration of CO₂ in seawater, there will be fluctuations in pCO₂ due only to changes in temperature.

Here is an informal argument for why this is true: At higher temperatures, CO₂ is less soluble in sea water. At equilibrium, partitioning of CO₂ between atmosphere and ocean water will shift more CO₂ to the atmosphere, thus raising the partial pressure of CO₂ in the atmosphere that equilibrates with the CO₂ in the water.

More formally, carbon dioxide (gas) in the atmosphere is in thermodynamic equilibrium with [CO₂] in the water, (where [CO₂] refers to the sum of activities of CO₂ and H₂CO₃ in solution).



Thus at equilibrium,

$$fCO_2 = [CO_{2(aq.)}]/K_0$$

where fCO_2 , the *fugacity* of CO₂, is “virtually equal to the partial pressure.” Unfortunately, K_0 is not constant, but depends on temperature and salinity. One model for that relationship is the following (From Weiss 1974 but also cited elsewhere):

$$\ln K_0 = -60.2409 + 93.4517(100/T) + 23.3585 \times \ln(T/100) + S * [0.023517 - 0.023656 * (T/100) + 0.0047036 * (T/100)^2]$$

(Note that temperatures need to be expressed in Kelvin)

Weiss, R. F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Mar. Chem., 2, 203-215.

What do those equations imply?

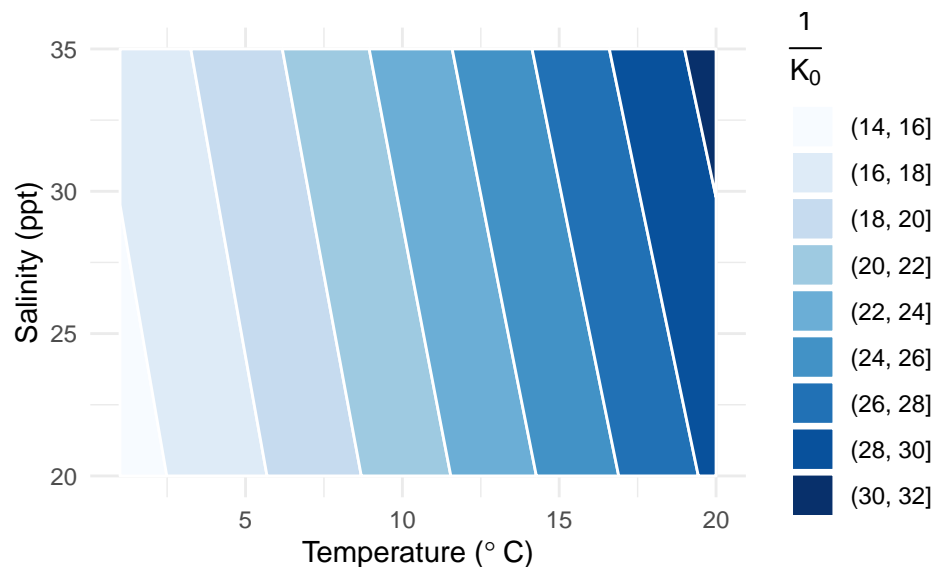
We will make a graphic that shows the magnitude of the conversion factor ($1/K_0$), which converts from observed $pCO_2 \approx fCO_2$ to $[CO_2]$ (from the second equation, above) over the range of temperatures and salinities we are mostly concerned with. This shows how measured pCO_2 will vary based on temperature and salinity alone – even without actual changes in the concentration of CO_2 .

```
library(readr)
library(tidyverse)

Tc <- seq(1,20,0.5)
S <- seq(20,35, 0.5)

test <- expand.grid(Tc=Tc, S=S) %>%
  mutate(T = Tc+273.15) %>%
  mutate(lnK = -60.2409 +
            9345.17/T +
            23.3585 * log(T/100) +
            S * (0.023517 -
                0.023656 * (T/100) +
                0.0047036 * (T/100)^2)) %>%
  mutate(K=exp(lnK), invK = 1/K)

ggplot(test, aes(x=Tc, y=S, z=invK)) +
  geom_contour_filled(color='white') +
  theme_minimal() +
  scale_fill_discrete(name = expression(frac(1, K[0])),
                      type = scale_fill_brewer) +
  xlab(expression('Temperature (*degree~C*~)')) +
  ylab('Salinity (ppt)')
```



Over the range of temperatures and salinities we are considering, the effect is mostly due to temperature – if only because temperatures vary over ~ 20 C, while salinities vary only from ~ 22 ppt to about 32 ppt. The overall effect of temperature and salinity could lead to a change in observed $p\text{CO}_2$ of about a factor of two.

Takehashi et al. 2002 Relationships

Takahashi et al. 2002 Used direct calculation of “temperature corrected” $p\text{CO}_2$ as a surrogate for changes in CO_2 concentration, and conversely, estimates of “expected” thermal $p\text{CO}_2$, as estimates of the magnitude of the fluctuations in $p\text{CO}_2$ one would expect to see due to temperature alone, if there were no changes in $[\text{CO}_2]$.

The Takehashi et al. 2002 equations are as follows:

“Expected $p\text{CO}_2$ ” at Observed Temperature

$$(p\text{CO}_2 \text{ at } T_{\text{obs}}) = (p\text{CO}_2)_{\text{obs}} \times \exp(0.0423(T_{\text{obs}} - T_{\text{mean}}))$$

“Temperature Corrected” $p\text{CO}_2$

$$(p\text{CO}_2 \text{ at } T_{\text{mean}}) = (p\text{CO}_2)_{\text{obs}} \times \exp(0.0423(T_{\text{mean}} - T_{\text{obs}}))$$

Equations from Takehashi et al. 2002 do not LOOK similar to Weiss’s equation, but they are nearly equivalent. At fixed salinity near full sea water, their predictions for observed $p\text{CO}_2$ essentially differ from what the Weiss 1974 equations predict only by a constant. This approximate equivalence might not be sufficient for careful work in the open ocean, but in the context of the large fluctuations in conditions in coastal estuaries, the inaccuracies will vanish amid other sources of variation.

Takahashi, Taro & Sutherland, Stewart & Sweeney, Colm & Poisson, Alain & Metzl, Nicolas & Tilbrook, Bronte & Bates, Nicholas & Wanninkhof, Rik & Feely, Richard & Chris, Sabine & Olafsson, Jon & Nojiri, Yukihiro. (2002). Global sea-air CO_2 flux based on climatological surface ocean $p\text{CO}_2$, and seasonal biological and temperature effects. Deep Sea Research Part II: Topical Studies in Oceanography. 49. 1601-1622. 10.1016/S0967-0645(02)00003-6.

Real Data

We use the Casco Bay data derived from the EPA collection of OA data from several NEPs. This data includes calculation of temperature corrected $p\text{CO}_2$. We chose these data to start from (rather than our own internal CBEP version of the data) for consistency, and to test code for use with other NEP datasets.

```
the_data <- read_csv("CB_oa_data.csv",
  col_types = cols(X1 = col_skip())) %>%
  mutate(Year = format(DateTime, format = '%Y'))
```

Temperature correction depends on temperature data

We have a couple of anomolous high temperature observations that appear to be outliers. They may represent a very low tide event on a hot summer afternoon, but I have not investigated further. I leave the data in the data, but note these values to make the point that corrected values depend on both accurate $p\text{CO}_2$ data and accurate temperature data.

```
a <- which(the_data$Temp_meas==max(the_data$Temp_meas, na.rm = TRUE))
the_data[(a-2):(a+2),]
```

```
## # A tibble: 5 x 10
##   WaterBody Season DateTime      Temp_meas Sal_meas CO2_meas DO_meas
##   <chr>      <chr> <dtm>          <dbl>    <dbl>    <dbl>    <dbl>
## 1 CB        Fall  2015-09-09 13:00:00    17.1      NA      767.    9.78
## 2 CB        Fall  2015-09-09 14:00:00    17.4      NA      728.   10.4
## 3 CB        Fall  2015-09-09 15:00:00    23.9      NA      639.   11.0
## 4 CB        Fall  2015-09-09 16:00:00    22.0      NA      617.    8.06
## 5 CB        Fall  2015-09-09 17:00:00    16.6      NA      704.    9.48
## # ... with 3 more variables: pH_meas <dbl>, CO2_Tcorr12 <dbl>, Year <chr>
```

```
rm(a)
```

Calculations

We calculate both the “thermal-only” and “temperature corrected” time series as calculated in Takehashi et al.

1. Calculate the expected thermal-only variation in $p\text{CO}_2$. This value (called “co2_thermal” here) is based on the average observed $p\text{CO}_2$. Since sampling is seasonally incomplete, this average is really just a reference value. The logic, however, is that if the molar concentration of CO_2 in the water column were constant, we would still see seasonal and diurnal variation in $p\text{CO}_2$, simply because the solubility of CO_2 is temperature dependent.
2. Calculate a “Temperature Corrected” $p\text{CO}_2$ value (“co2_corr”). This is the converse of (1.). Here it provides a trace of changes in $p\text{CO}_2$ that “would have happened” in the absence of temperature changes. These reflect changes in the concentration of CO_2 , which reflect a combination of biology and diffusion of CO_2 between ocean and atmosphere and advection past the sensor suite by tides and currents. Here we adjust $p\text{CO}_2$ to a “standard temperature” of 12 degrees C. This is slightly warmer than our observed average temperatures, and matches the temperature average used temperatures. Results should exactly match the value of CO2_Tcorr12.

The logic is that if there were no biology (and no advection or diffusion between surface waters and the atmosphere), then `co2_meas` would equal `co2_thermal`, and `co2_corr` would be a flat line (within measurement error). Neither is the case (see graphics, below) providing strong evidence that CO₂ behavior in Casco Bay is influenced by system metabolism.

```
t_ref = 12
(t_mean = mean(the_data$Temp_meas, na.rm=TRUE))
```

```
## [1] 11.49358
```

```
(co2_mean = mean(the_data$CO2_meas, na.rm=TRUE))
```

```
## [1] 578.2843
```

```
the_data <- the_data %>%
  mutate(co2_thermal = co2_mean*exp(0.0423*(Temp_meas-t_mean))) %>%
  mutate(co2_corr = CO2_meas*exp(0.0423*(t_ref-Temp_meas)))
```

Thankfully, our calculations of temperature corrected pCO₂ (`co2_corr`) match the values in the data from EPA (CO₂_Tcorr12).

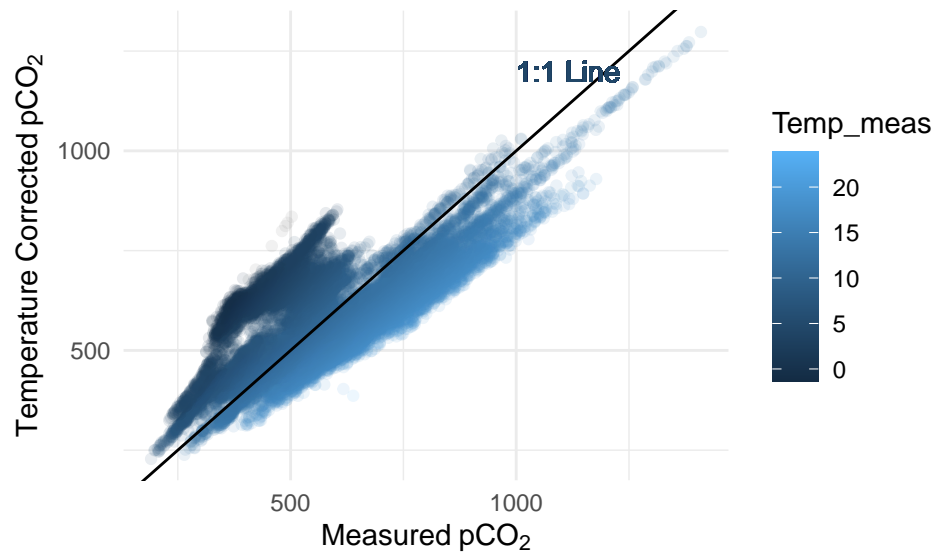
The average temperature in our data is about 11.5C, partly because we have relatively little winter data. More interesting, the average observed pCO₂ is about 575 micro-atmospheres – well above atmospheric averages of about 400 micro-atmospheres.

A quick check shows that the calculations in (2.), above, produced data that is linearly related to the calculations of [CO₂] we ran based on the thermodynamic equilibria. These two ways of thinking about temperature dependence of pCO₂ or [CO₂] will give (nearly) identical results (subject only to a scaling factor).

Exploratory Graphics

The following graphics show how the Takahashi et al. corrections look in Casco Bay.

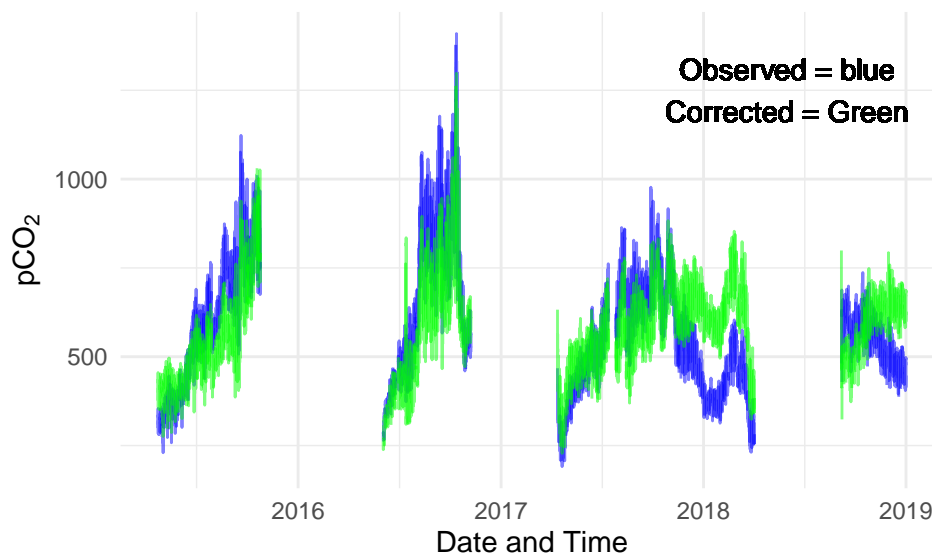
```
ggplot(the_data, aes(x=CO2_meas, y=CO2_Tcorr12, color = Temp_meas)) +
  geom_point(alpha = 0.1) +
  geom_abline(slope = 1, intercept=0) +
  geom_text(aes(x=1000, y=1200, label = '1:1 Line'), hjust = 0) +
  xlab(expression(Measured~pCO[2])) +
  ylab(expression(Temperature~Corrected~pCO[2])) +
  theme_minimal()
```



Conceptually, the “correction” is adjusting for the natural effect of solubility on pCO₂. Since pCO₂ is higher at higher temperatures (CO₂ is less soluble) the correction RAISES the value at low temperatures, and it LOWERS the value at high temperatures.

Overall it reduces apparent swings in pCO₂, as the next plot confirms.

```
ggplot(the_data, aes(x=DateTime)) +
  geom_line(aes(y=CO2_meas), color='blue', alpha = 0.5) +
  geom_line(aes(y=CO2_Tcorr12), color = 'green', alpha = 0.5) +
  xlab('Date and Time') +
  ylab(expression(pCO[2])) +
  geom_text(aes(x=as.POSIXct('2018-06-01'), y=1250, label='Observed = blue\nCorrected = Green')) +
  theme_minimal()
```

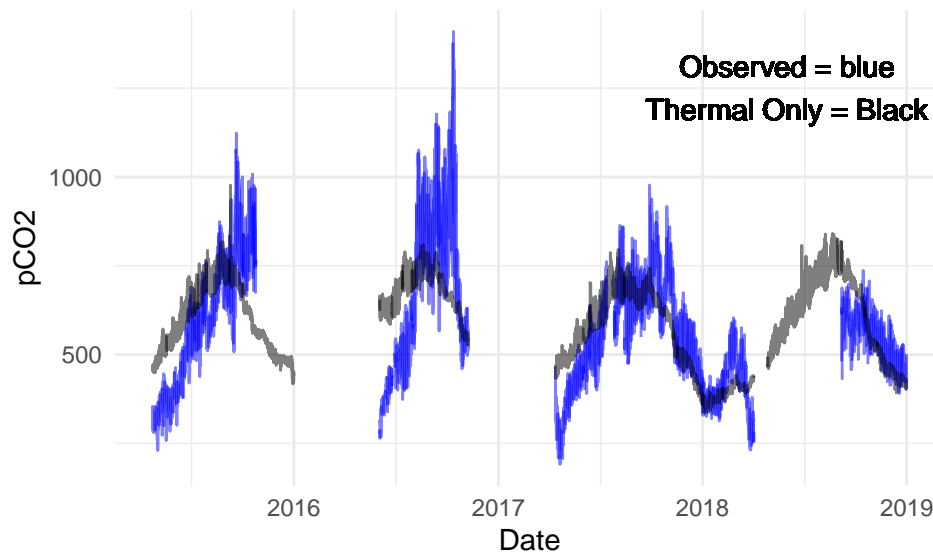


The net effect is to somewhat flatten out the seasonal swings in CO₂. Diurnal swings look less affected, although that is hard to evaluate from this plot.

If there were no biology, what would we see?

Here we compare predicted based on temperature alone, versus what we actually observed.

```
ggplot(the_data, aes(DateTime, group = Year)) +  
  geom_line(aes(y=CO2_meas), color = 'blue', alpha = 0.5) +  
  geom_line(aes(y=co2_thermal), alpha = 0.5) +  
  geom_text(aes(x=as.POSIXct('2018-06-01'), y=1250, label='Observed = blue\nThermal Only = Black')) +  
  theme_minimal() +  
  xlab('Date') +  
  ylab('pCO2')
```



In spring we see pCO₂ levels well below what we would expect only due to temperature, while by late summer and fall, water temperatures are beginning to drop again, but pCO₂ stays high. Also, it looks like diurnal fluctuations in pCO₂ are substantially greater than would be predicted based on temperature alone.

That suggests: 1. biological activity is removing CO₂ from the water column in the spring, and returning it to the water column in the late summer and fall. 2. Biological activity, perhaps related to photosynthesis, magnifies diurnal patterns.