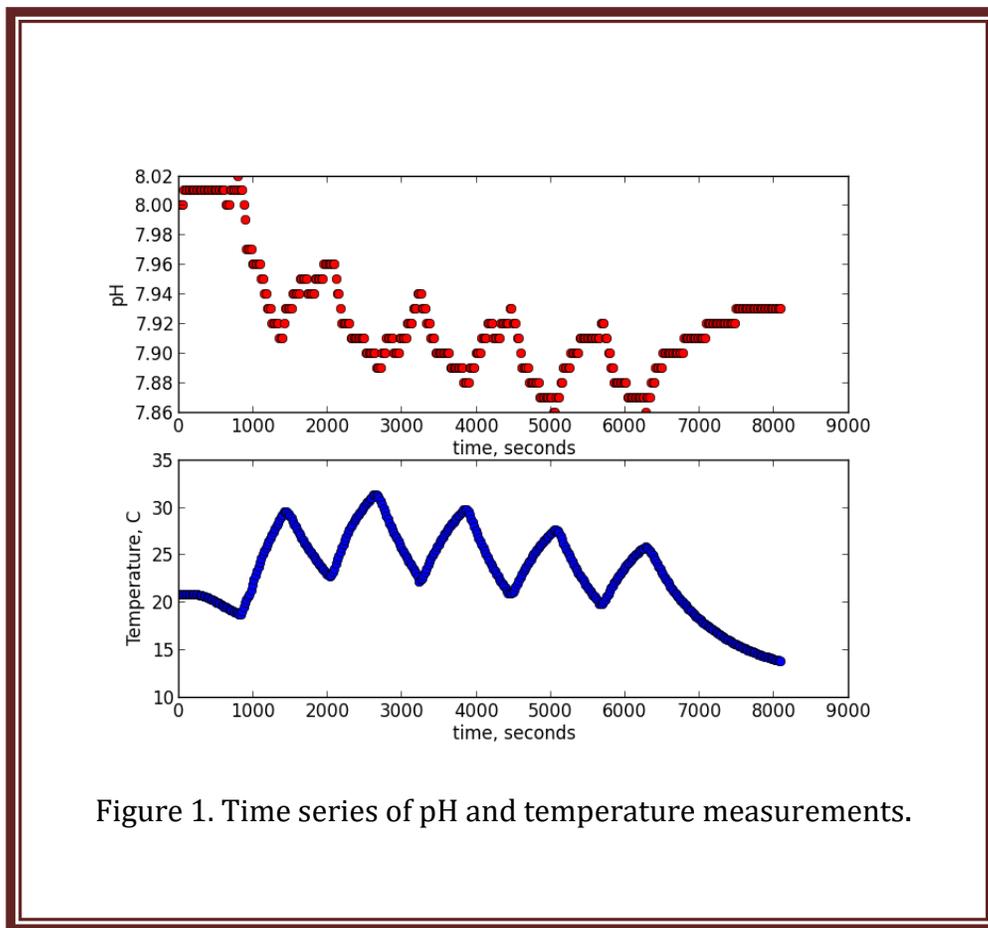


EXO pH and Temperature

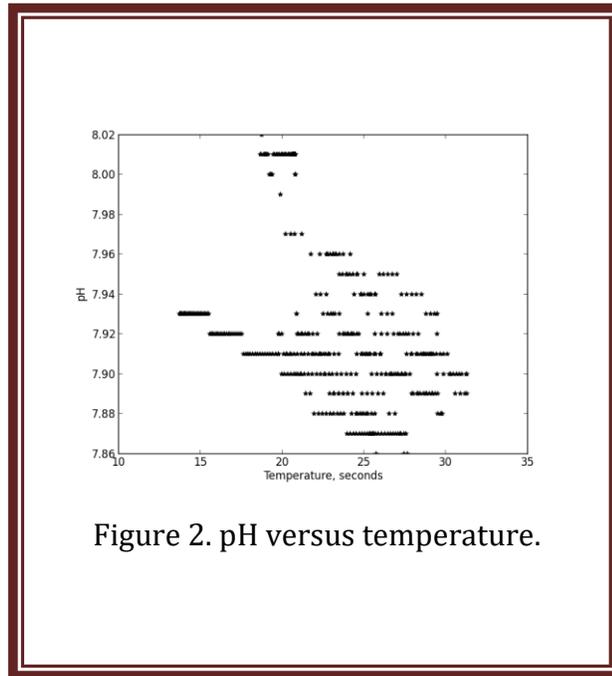
A correlation apparent between pH and temperature in the field suggests that there may be temperature contamination in the pH measurement made by the EXO sonde. The following experiment was performed to understand the effects of temperature on the sonde pH measurements.

We examined this issue using the calibration cup on the sonde filled with water from Alamitos Bay, which should be a good representation for sea water. The sonde was alternately immersed in warm and cool water. Hence, the sonde will be testing the same water, but at different temperatures. The pH sensor was calibrated using the 7 and 10 pH buffers. Then the sonde was deployed to sample every 20 seconds, and it was moved between cool and warm buckets of water every 10 minutes for 5 cycles. Then the sonde was left in the cool-water bucket for 30 minutes. The time series for both pH and temperature are shown in Figure 1.



There is a clear modulation in the pH, being anti-correlated with the temperature (i.e., higher temperatures produce more acidity). There is about 0.05 pH units per 6 degree change in temperature.

However, there is a noticeable long-term drift in the pH as it starts at 8.01 for a temperature of ~20° C, but is 7.92 when the temperature is 20° C near the end of the experiment. That is 0.1 pH unit. We cannot rule out that the sea water was chemically unstable during this time as it must contain organic material. This drift provides the rather unorganized scatter plot shown in Figure 2.



The modulation results appear consistent with the pH values parameterized by temperature on the calibration buffers. These are shown in Table 1.

Table 1. Buffer label pH and temperature

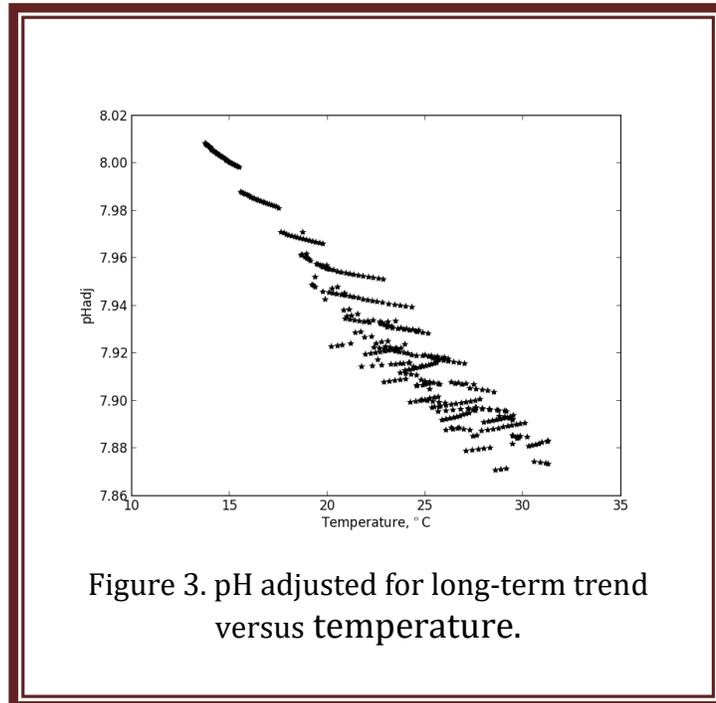
Temperature, C	pH 10 buffer	pH 7 buffer	pH 4 buffer
15°	10.12	7.05	4.00
20°	10.06	7.02	4.00
25°	10.00	7.00	4.00

From Table 1, buffer 10 gradient is -0.012 pH/°C, buffer 7 gradient is -0.005 pH/°C. and buffer 4 gradient is 0 pH/°C. Interpolating the buffer gradients suggests that the gradient of buffer 8 is -0.0073 pH/°C and that for buffer 9 is -0.0096 pH/°C.

The sample yields a gradient of -0.007 pH/°C, which is the average gradient between the 5 peaks and 4 troughs existing between 1300 seconds and 6500 seconds (Figure 1) and having values between 20° C and 30° C. This is the same gradient value derived from expectations from the buffer labels and consistent with expectations of ion activity.

This calculation was elaborated by removing the trend in pH with time. The slope of pH/seconds was estimated using the pH value at 500 seconds (temperature = 20.105, pH = 8.01)

and 6800 seconds (temperature = 20.156, pH = 7.90). Using only the data from 500 seconds onward, a new scatter plot of the adjusted pH vs temperature was made and shown in Figure 3. The data now appear much more organized. The change in pH with temperature at a pH of



approximately 8 is $-0.007/^{\circ}\text{C}$.

We conclude that the pH temperature gradient for pH values near that of sea water is $-0.007 \text{ pH}/^{\circ}\text{C}$ for temperatures between 15°C and 25°C , with colder water producing more basic values. This characteristic is consistent with expectations for hydrogen ion activity varying with temperature. This value for the gradient is in line with the published results for the calibration buffers which indicate the gradient increases in magnitude for increasing pH. There appeared to be a longer term trend in the measured pH of the sample, but the stability of the sample of natural sea water is unknown.