March 9, 2015

Dear Billy,

Thank you for your questions. I feel rewarded to hear these questions, which reflect that you thought about the observations. Since I did not discuss the complexity of CO2 chemistry in oceans in my presentation, I wish to clarify and answer your questions in writing.

In your questions, which are reproduced here, I see three components, which I marked with the parentheses: "(1) *Your maps of surface pH show that in the temperate north Pacific pH is lower in the warm months by a small amount.* (2) *Yet carbon dioxide dissolves better in colder seawater.* (3) *And if I understand correctly, deeper, colder water is more acidic. So, why is the warmer surface water a little more acidic?*"

(1) As you observed, the 2005 map for the North Pacific shows that the pH of the temperate ocean water is about 8.04 (blue, more acidic) in August (warm), whereas that in the colder February water is about 8.12 (green, less acidic). This is primarily due to the competition of two effects: temperature effect and photosynthesis. The H+ concentration in seawater increases with warming (i. e. becomes more acidic or lower pH) as will be explained below. This is opposed by the effect of photosynthesis, which should make water less acidic by drawing down CO2 from seawater.
For example, in the Hawaii area, the temperature of surface waters is 25°C on the annual mean, and it changes seasonally by 3 °C above and below the mean. Based on precise chemical studies, we know that 1°C warming should cause a change of -0.016 pH per °C (acidification), ***if the total CO2 concentration in seawater is kept constant.*** Accordingly, a 3 °C warming should cause a decrease in pH of 0.05 pH (or an increase in H+ of about 12%). This is in agreement with the observed seasonal pH decrease of 0.05 in summer months. As you see in the time-series plots, the total CO2 concentrations and alkalinity did not vary much seasonally, indicating low levels of photosynthetic activities. Hence, the seasonal pH changes in the Hawaii area are regulated by temperature changes.

In the Bermuda area, the seasonal changes in water temperature (8°C above and below the mean of 23°C) are much larger than Hawaii, so as the biological activities. The observed pH decrease in summer months is 0.01 pH, and the respective effects of temperature and biology on seawater pH are as follows.

pH change due to warming (8 °C warming) =	-0.14
pH change due to biological drawdown of CO2 =	+0.09
pH change due to decreased alkalinity (rain and biology) =	-0.05
Total effect on pH ………………………………	-0.10 (more acidic in summer)

Note that the temperature effect is partially cancelled by photosynthesis effect. In contrast, the biological effect overtakes the temperature effect in polar waters,.

(2) Another question is "*Why does warming cause lower pH, in spite of the fact that solubility decreases with warmer temperatures?*" You are pointing out that less CO_2 in warmer waters should make the water less acidic rather than more acidic (lower pH) . We need to consider two processes to answer this question. First, when temperature of water is increased, pCO_2 (= the vapor pressure of CO_2) in water increases very rapidly because of the reduced solubility of CO_2 in water. This causes loss of CO_2 from the water to air as observed rising bubbles in warm soda. The loss of carbonic acid (or CO_2) results in the loss of acidity and the water becomes less acidic (i. e. increase in pH) or more alkaline. On the other hand, if CO_2 is not allowed to escape and the total amount of CO_2 dissolved in water is unchanged, pH of seawater should become more acidic as the water is warmed (by -0.016 pH per °C in normal seawater). Therefore, the response of the pH of seawater to warming is determined by the competition between the rate of warming and the rate of loss of CO_2. Since warming is commonly associated with greater photosynthesis in the real ocean, the acidification effect by warming is counter-acted by the alkalization by biology. However, the warming effect is dominant in temperate oceans where seasonal temperature changes are large and biological production is low; whereas, in the polar waters, biological effect far exceeds the temperature effect.

3) " …*deeper, colder water is more acidic. So, why is the warmer surface water a little more acidic?*" Deeper waters are rich in CO_2 and nutrients (phosphate, nitrate and silicate ions) produced in deep waters by microbial oxidation of biological debris raining down from the productive photic zone of the oceans. They are more acidic (pH ~7.5) because of the high CO_2 concentrations. When the deep water upwelled to the surface and is exposed to the air and the sun, it loses CO_2 to air because of its high pCO_2 produced by warming, and hence becomes less acidic due to reduced CO_2 concentrations. Photosynthesis further reduces the CO_2 concentrations, resulting in further increase in pH and degree of $CaCO_3$ saturation. In this case, the effect of CO_2 loss on pH overwhelms the temperature effect. The upwelled waters may eventually become less acidic than the surrounding surface waters after intense plankton blooms.

Influx of newly upwelled acidic deep waters to the Oregon coast would have devastating effects on oyster larvae. Increase in pH by the photosynthetic draw down of CO_2 and de-gassing to the air in coastal oceans would create favorable conditions for the growths of baby oysters.

I hope that I explained your questions,

Taro