pH vs Alkalinity

Most Fish Keepers surely have heard something called pH and some may even have heard the word Alkalinity being thrown to add confusion to this supposedly “simple hobby”. One main difference between keeping fish to other land animals is that we, as the keepers, need to create and control every aspects of their environment so it is suitable for our Koi to thrive. Dog breeders never have to worry whether there is enough air for their dogs to breath, or whether the garden the dogs are playing has acidic or alkaline grass. We, Koi Keepers, do.

This article is an attempt to discuss 2 of the many aspects of Koi Keeping that we need to understand in order to control them properly. We will have to go into the realm of water chemistry…, well, luckily the author has David Hemenway, who is Full Professor in the Department of Civil and Environmental Engineering in Vermont, that clearly explain this to the author and now sharing this knowledge to benefit us all.

Let’s start with CO2.

CO2 dissolves in water to form carbonic acid according to the following equation.

$$CO_{2-gasphase} \Leftrightarrow CO_{2-dissolved} + H_2O \Leftrightarrow Carbonic\ Acid\ or\ H_2CO_3$$

Importantly (first fact I didn’t know), this process is not instantaneous, but happens according to a straightforward physical law (called Fick’s law). Also (2nd new fact to me) in much of the world, at a temperature of 25 degrees C, the saturation constant of CO2 in water is approximately 0.5 mg/L. What this means is that a body of water in communication with the atmosphere will in time acquire a concentration of 0.5 mg/L dissolved CO2.

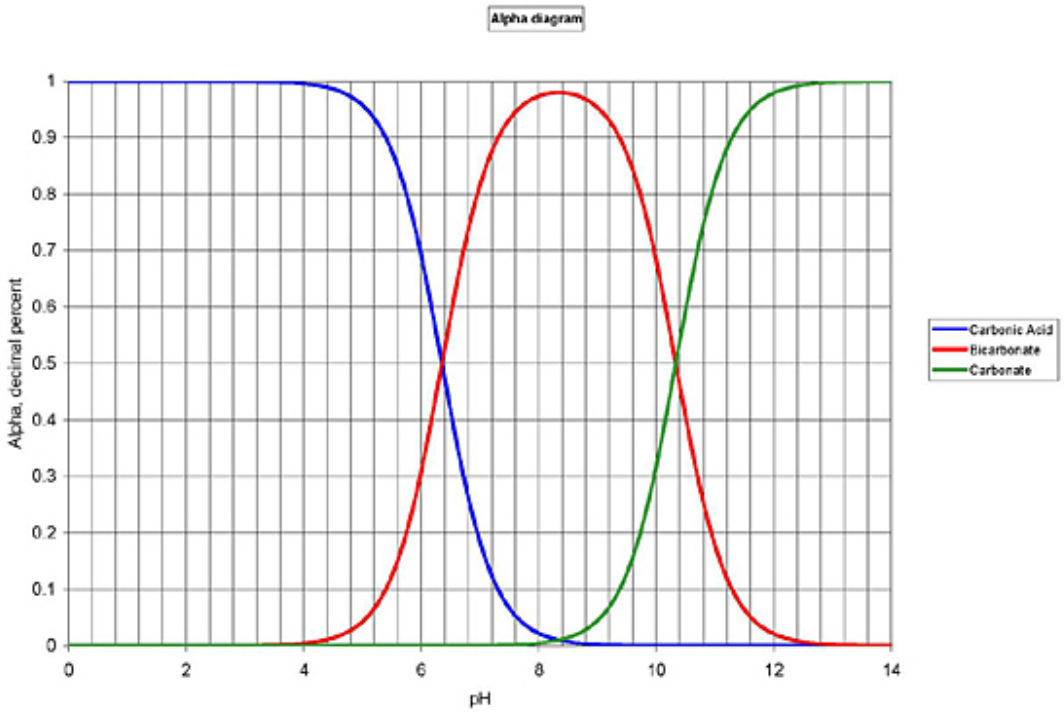
From here on, I will stop pointing out the facts I didn’t know previously, as this may (a) make it difficult to follow and (b) make me seem very stupid.

To continue on, carbonic acid can lose two hydrogen ions to form bicarbonate and then carbonate. This can be written as follows.

$$equa.1 \quad H_2CO_3^* \Leftrightarrow H^{+1} + HCO_3^{-1} \quad the\ bicarbonate\ ion\ further\ ionizes\ as\ follows:$$

$$equa.2 \quad HCO_3^{-1} \Leftrightarrow H^{+1} + CO_3^{-2}$$

Now for the first really interesting bit. The proportion of carbonic acid to bicarbonate to carbonate varies according to pH. The relationship is shown on the following graph, called an alpha diagram.

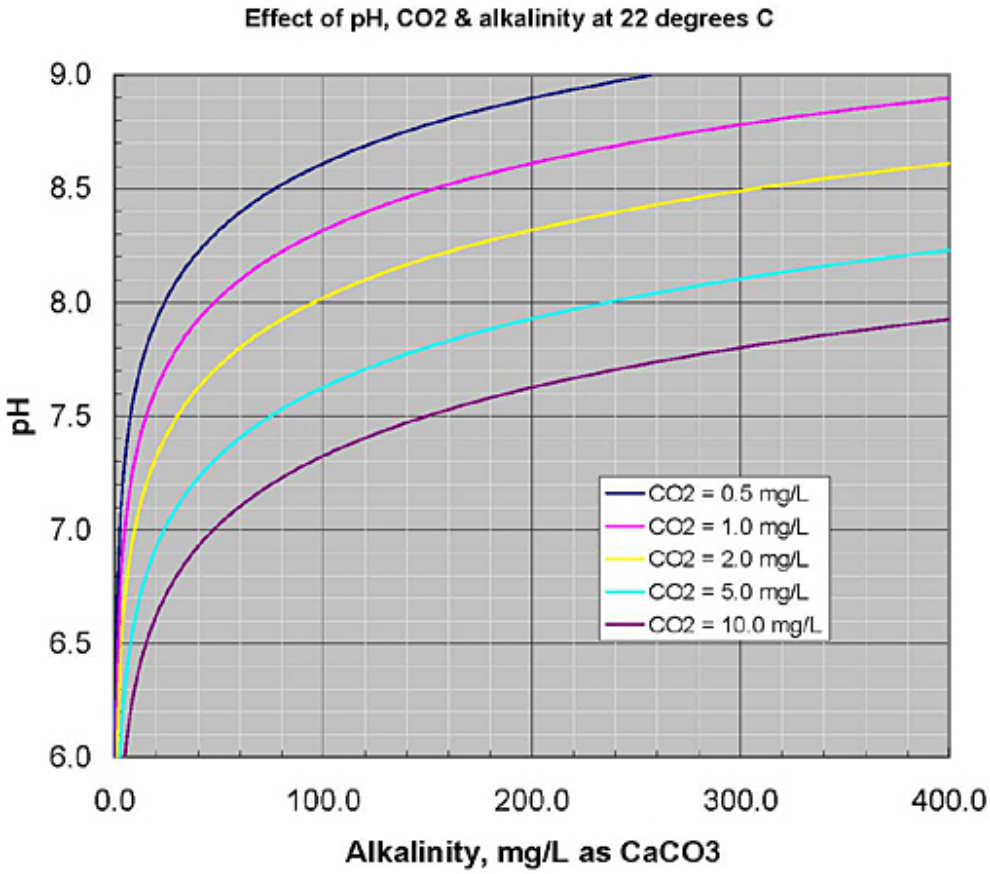


What this diagram shows is that for the pH range present in our ponds, virtually all of the carbonic acid/bicarbonate/carbonate is present as bicarbonate.

Alkalinity is a measure of the resistance of (in our case pond) water to a reduction in pH when hydrogen ions are added. Any weak acid or base can act as a buffer, including hydrogen sulfide, acetic acid, the phosphoric acid system, carbonate (or carbonic acid system), ammonia, and so on. But in a pond the carbonate/carbonic acid system is essentially the only buffering system available, and it accounts for >98% of the buffering in the normal pH range of ponds.

It is for purely historic reasons that alkalinity is expressed as mg/L of $CaCO_3$. But do not be mislead into thinking that this means there is actually any significant amount of carbonate (CO_3) dissolved in your pond water!

The next very interesting fact is the fixed relationship between CO_2, alkalinity and pH. This is set according to the following graph, which shows (at 22 degrees C – the temperature of my pond at present) the pH for any alkalinity value depends upon the level of dissolved CO_2. This graph is similar to others available on the web and elsewhere, but has the advantage of showing the 0.5 mg/l CO_2 line. This and all the other lines are from data calculated for my own pond temperature.



What this graph shows is that far from being totally unrelated, the pH depends upon the alkalinity for any level of dissolved CO2 at a particular temperature. So the idea that alkalinity is completely separate from pH (which is by 'coincidence' called either acid or alkaline) is a myth. The two are tightly connected.

At 22 degrees C, then, if a pond has an alkalinity of 100 and a pH of 7.6, the dissolved CO2 will be about 5.0 mg/L. As I understand it, this is a chemical fact.

Since a body of (uninhabited) water in communication with the atmosphere will normally have a CO2 concentration of 0.5 mg/L, this means that a body of water with a pH of 7.6 at an alkalinity of 100 must have a CO2 level significantly above saturation (i.e., it is supersaturated with respect to CO2). If this excess CO2 is removed then the pH must be driven up. It is Fick's law (mentioned above) which stops the CO2 from dropping below 0.5 mg/L and which limits the speed of transfer of CO2 into, or in this case out of solution. Even with air domes and trickle towers etc. running, Fick's law still governs the transfer of CO2 from the fish and microbial respiration out of the water, but this rate of transfer is not instantaneous and the effect is that the CO2 level in the pond remains higher than the 0.5 mg/L saturation limit of uninhabited water.

Until a few days ago my pond contained a great deal of blanket weed. I ordered a CO_2 test kit to try and understand what was going on better. The day the test kit arrived (29th July), I measured the CO_2 level at 6pm and it was 1.8. My alkalinity was 84 and my pH was 8.4. I repeated the measurement at 11pm and the CO_2 was 3.0 mg/L. Just as this graph predicts, my pH had reduced to 7.8. Next morning at 8am the CO_2 level was 5 mg/L and the pH had dropped slightly further to 7.6.

That afternoon I put some stuff in the pond to kill the blanket weed. Within 24 hours (at 8:30am) my measured CO_2 had climbed to 17 and (as you might guess from this graph) my pH had dropped to 7.1. At 6:30pm 1st August my CO_2 was 14.5 mg/L and pH 7.3. On 2nd August at 4:45pm my CO_2 was 10.5 mg/L and pH 7.4.

Now the CO_2 test kit (Hanna HI-3818) is a titration kit and I do not claim it is 100% accurate or that I am particularly good at using it. (also CO_2 is difficult to measure accurately since it can be transferring into or out of solution while you are titrating). But the measurements I have taken as the blanket weed has been dying off, and hence its photosynthetic activity has been declining, do show a rise in CO_2. The alkalinity in my pond has not changed and nor has the temperature. And the pH levels have approximately matched those predicted by the graph above according to the changing CO_2.

This is only part of the story.

But I no longer believe that alkalinity is just a way of buffering against pH change with addition of hydrogen ions. The two are much more tightly linked than I had been led to believe.

Hope this makes sense to someone out there. All the information is thanks to David Hemenway. All the mistakes are thanks to me.

Guy Sawle