Alkalinity
Alkalinity is a measure of all the materials in water that can resist a change in pH when acid is added. They provide a buffering capability. The addition of an acid into the water places a stress on its aquatic life / equilibrium system. However, alkalinity describes how well a stream, river, or lake can recover from an "acidic" punch.

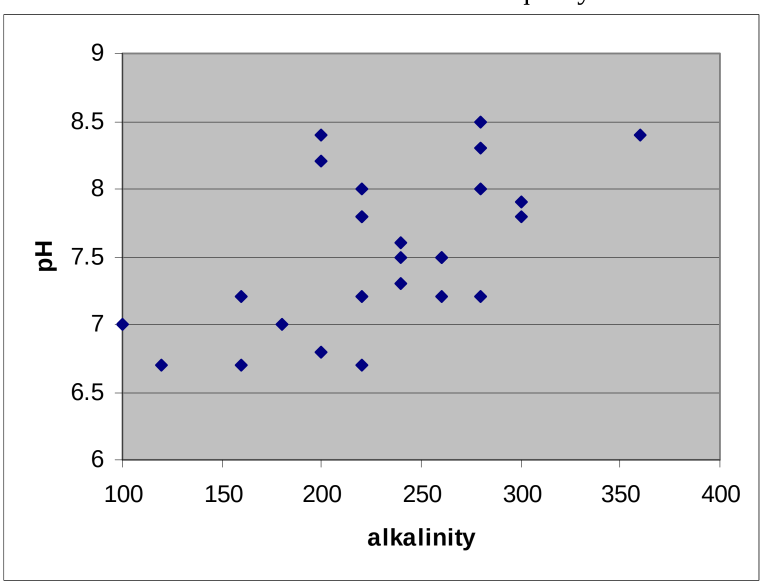
The measurement is the stoichiometric summation of several components in the water (mainly bicarbonate, carbonate, and hydroxide) that tend to elevate the pH of the water above 4.5. Other substances like phosphates, silicates, and nitrates can contribute also. Alkalinity is typically expressed in mg/L of calcium carbonate ($CaCO_3$) because calcium carbonate is a good acid neutralizer. Water with low alkalinity has a low capacity to neutralize or "buffer" incoming acids and is, therefore, very susceptible to acidic pollution. In contrast, water with greater alkalinity or buffering capacity, will have the ability to neutralize more of the incoming acidity and, therefore, resist rapid changes in pH.

A stream's alkalinity is influenced by rocks and soils, salts, some plant activities, and certain industrial wastewater discharges. In Pennsylvania, a significant amount of the ground water passes through limestone, which contains calcium carbonate ($CaCO_3$). If the ground water picks up the carbonate ions, it possesses an alkalinity to neutralize against incoming acid.

The acid can come from rain, where 'pure rain' has a pH of 5.6. Acid rain is even more acidic since it has byproducts of power plants. Acid can also be produced by bacteria within certain aquatic systems. Water exiting from a mine is another source for acid addition into a stream. The acid is produced through the weathering of pyrite which was exposed from the mining operation. (It has been stated that mine drainage is the second largest water pollution problem in Southwestern Pennsylvania.)

Well-buffered surface water systems have alkalinity values of 20 to 300 mg/L. An alkalinity above 75 mg/L is recommended to offset acid produced by bacteria which nitrifies ammonia.

Looking at data from the Lick Run location, the direct relationship between pH and alkalinity is visible. When the alkalinity is low, there is less neutralizing ability, and pH values are below 7. The Lick Run stream runs near an old stone quarry.



Comparing the alkalinity data from several PaSEC monitoring teams with their external lab measurements show a bias. The PaSEC analyses were nearly always higher by 13+ %.

			PaSEC	external				
team	external		mg / L	mg / L	difference in analysis	RPD %	difference in analysis	RPD %
a	x		20	21	-1	5		
a	x		220	224	-4	2		
a	x		20	11			9	58
b	x		260	219	41	17		
c	y		65	57	8	13		
c	y		160	99			61	47
d	y		75	57	18	27		
d	y		170	99			71	53
e	y		240	186	54	25		
		average	**137**	**108**				
		range	20 - 260					

overall RPD ave = 27.4 %
RPD = Relative Percent Difference

observations PaSEC readings are almost always higher
every team with multiple samples had one off by ~50%

The RPD target per QAPP is 20% on the same sample.

The alkalinity test is one of neutralization. The difference might be the titrating end-point was overshot during the PaSEC analyses. The analysis procedure notebook states to "add acid until the sample turns pink". I know one team (ours) adds acid until we no longer see a change in color. This equates to a light pink. Checking with the Pa DEP, Cheryl Snyder responded - “HACH … told us to titrate the alkalinity test until we saw a color change from blue to purplish pink. The purplish pink color was the first color change. Continued titrating results in a lighter pink color. I think there are actually two endpoints in this test and it sounds like you were going to the second endpoint. Try going to the darker purplish pink color and see if you get closer results to the lab. “

The majority of these analyses can be done with the 20-400 range alkalinity testing procedure. In this procedure, each drop of acid (x20) equates to 20 mg/L in the final result. For a 200 mg/L final, one extra drop results in a 10% change in the reading. For a 100 mg/L test, one extra drop results in a 20% change (the maximum RPD objective). Cheryl added “you could also check your field kit results against the digital titrator test for alkalinity. The digital titrator provides a smaller drop size as compared to the eyedropper which allows you to get a little closer to the correct result. You would still need to go to the darker purplish pink endpoint in the titration.”

Alkalinity can be higher in the warmer months of the year as there is the potential for increased solids solubility in the water due to the higher temperatures. For the Lick Run data, the May-Oct period averaged 252 mg/L, and the Nov-Apr period calculated to 182 mg/L.

jmm
1/08