Alkalinity

Summary
Alkalinity is a measure of "acid neutralizing capacity." Low alkalinity can result in rapid pH changes, if acid or base enters the water. Streams and lakes west of the Cascade Mountain Range typically have low alkalinity (<100 mg/L $CaCO_3$) because of the volcanic geology.

Sources
The primary source of alkalinity is carbonate-containing rocks, which can come from:
- Natural erosion of carbonate-containing "limestone," such as calcium carbonate or dolomite;
- Runoff from agricultural or other landscapes where "lime" has been applied.

Alkalinity is a measure of the capacity of water or any solution to neutralize or "buffer" acids. This measure of acid-neutralizing capacity is important in figuring out how "buffered" the water is against sudden changes in pH.

Alkalinity should not be confused with pH. pH is a measure of the hydrogen ion (H^+) concentration, and the pH scale shows the intensity of the acidic or basic character of a solution at a given temperature. The reason alkalinity is sometime confused with pH is because the term *alkaline* is used to describe pH conditions greater than 7 (basic).

The most important compounds in water that determine alkalinity include the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. Carbonate ions are able to react with and neutralize 2 hydrogen ions (H^+) and the bicarbonate ions are able to neutralize H^+ or hydroxide ions (OH^-) present in water. The ability to resist changes in pH by neutralizing acids or bases is called buffering.

Alkalinity is important to aquatic organisms because it protects them against rapid changes in pH. Alkalinity is especially important in areas where acid rain is a problem.

Table 1. *Important compounds for alkalinity.*

H^+	Hydrogen ion (acid)
OH^-	Hydroxide ion (base)
H_2CO_3	Carbonic acid
HCO_3^-	Bicarbonate ion
CO_3^{2-}	Carbonate ion
$CaCO_3$	Calcium carbonate (calcite)
$CaMg(CO_3)_2$	Dolomite lime

Sources

One source of alkalinity is calcium carbonate ($CaCO_3$), which is dissolved in water flowing through geology that has limestone and/or marble. Limestone is a sedimentary rock formed by the compaction of fossilized coral, shells and bones. Limestone is composed of the minerals calcium carbonate ($CaCO_3$) and/or dolomite ($CaMg(CO_3)_2$), along with small amounts of other minerals. Limestone is converted to marble from the heat and pressure of metamorphic events.

Mountain lakes fed directly by snowmelt usually have very low alkalinity, since the water feeding them doesn't have much time to interact with the geology. Volcanic rock, such as basalt, erodes very slowly and is very low in buffering minerals. Most

streams in western Oregon and Washington have low alkalinity due to the volcanic geology of the Cascade Mountain Range.

> Alkalinity can increase the pH (make water more basic), when the alkalinity comes from a mineral source such as calcium carbonate ($CaCO_3$). When $CaCO_3$ dissolves in water, the carbonate (CO_3^{2-}) can react with water to form bicarbonate (HCO_3^-), which produces hydroxide (OH^-):
>
> $$CaCO_3\ (s) \leftrightarrow Ca^{2+} + CO_3^{2-}$$
>
> $$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$$
>
> The hydroxide ion (OH^-) is a strong base. An increase in OH^- concentration will cause the pH to increase.

In addition to rocks and soils, the alkalinity of streams can be influenced by

- salts,
- plant activity, and
- wastewater.

Wastewater can have higher alkalinity because it typically has higher concentrations of nutrients and ions, some with acid buffering properties, such as silicates and phosphates.

Stormwater runoff leading to streams can carry lime (either calcite or dolomite), which is applied to lawns and agricultural fields. Clay soils naturally have an acidic pH (~pH 4-6), and ammonia-based fertilizers produce acid as they are decomposed:

$$(NH_4)_2SO_4 + 4\ O_2 \rightarrow 2\ HNO_3 + H_2SO_4 + 2\ H_2O$$

Lime is often added to increase soil pH and buffer soil and fertilizer acids.

In watersheds where calcium carbonate isn't available, carbonic acid is an important source for carbonate and bicarbonate. Carbon dioxide and water are converted to carbonic acid through the following reaction:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \text{ (carbonic acid)}$$

Carbonic acid provides bicarbonate and carbonate for buffering, just like $CaCO_3$:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

While conversion of carbon dioxide to carbonic acid produces ions capable of buffering pH, it also causes a decrease in pH (increase in H^+) that $CaCO_3$ doesn't. Notice in the reaction that as carbonic acid (H_2CO_3) reacts to form carbonate (CO_3^{2-}), 2 hydrogen ions (H^+) are released into the water.

Table 2. *Typical alkalinity ranges.*

	(mg/L $CaCO_3$)
Rainwater	<10
Typical surface water	20 – 200
Surface water in regions with alkaline soils	100 – 500
Groundwater	50 – 1000
Seawater	100 – 500

Measurement

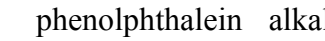
Total alkalinity is measured by titrating (step-wise addition of reagent) the water sample with sulfuric acid (H_2SO_4) to a pH endpoint of ~4.5. Once the water sample reaches a pH of 4.5, the three main forms of alkalinity (bicarbonate, carbonate, and hydroxide) have been neutralized.

When titrating for total alkalinity, there are 2 "equivalence points," where pH changes rapidly with small additions of acid – these lie near pH 8.3 and 4.5. These points can be determined by measuring pH as the acid is added, or by choosing indicators that change color at the pH value of the equivalence point.

The Alkalinity Test

Step 1: Phenolphthalein Alkalinity

For solutions at pH 8.3, bicarbonate is the predominant carbonate species:

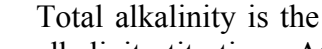


$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

Phenolphthalein is an indicator that changes from pink to colorless at pH 8.3 when acid is added (pH decreases). Water that has a pH >8.3 is said to have "phenolphthalein alkalinity," which is alkalinity due primarily to the presence of carbonate or hydroxide ions. Many water samples have little or no phenolphthalein alkalinity, and therefore remain colorless after adding this indicator to the sample water.

Step 2: Total Alkalinity

Total alkalinity is the final endpoint for the alkalinity titration. At pH 4.5, all carbonate and bicarbonate ions have been converted to carbonic acid (H_2CO_3):



$$HCO_3^- + H^+ \rightarrow H_2CO_3$$

This endpoint for the titration can be identified using a Bromcresol Green-Methyl Red indicator. The indicator changes from green to pink at pH 4.5.

Below pH 4.5, the water is less able to neutralize the sulfuric acid and there is a direct relationship between the amount of sulfuric acid added to the sample and the change in the pH of the sample.

Units

To standardize reporting, alkalinity is typically reported in units of "mg/L as $CaCO_3$." Even though streams west of the Cascades have little to no $CaCO_3$, alkalinity results reported as $CaCO_3$ can be directly compared to any other stream in the country.

Why is alkalinity reported as "mg/L as $CaCO_3$"?

Units of mg/L are a "mass dissolved in a liquid." Reporting alkalinity as "mg/L as $CaCO_3$" specifies that the sample has an alkalinity equal to that of a solution with a certain amount of calcium carbonate ($CaCO_3$) dissolved in water. The alkalinity test does not actually measure a mass per volume.

Alkalinity, or "acid neutralizing capacity," is measured by adding acid to the sample and figuring out the equivalent alkalinity in the water. The actual units for the alkalinity titration are moles or equivalents per volume (moles/L or eq/L). Converting alkalinity from eq/L to "mg/L as $CaCO_3$" takes into account that one mole of carbonate (CO_3^{2-}) can neutralize 2 moles of acid (H^+).

$$\text{Alkalinity } \frac{\text{eq}}{\text{L}} * \frac{1 \text{ mol } CaCO_3}{2 \text{ eq}} * \frac{100.09 \text{ g } CaCO_3}{1 \text{ mol } CaCO_3} * \frac{1000 \text{ mg}}{1 \text{ g}} = \text{Alkalinity (mg/L as } CaCO_3)$$

The units of "mg/L as $CaCO_3$" are for convenience only, allowing you to consider how much $CaCO_3$ you would need to create a solution with the same alkalinity as your sample.