Hardness

What is hardness?

Hardness is a measure of all multivalent cations (ions with a positive charge greater than +1) present in solution. Ca^{2+} (calcium) and Mg^{2+} (magnesium) are the most common multivalent cations in fresh water. A simplified definition of hardness is the amount of dissolved calcium and magnesium in the water.

Geology is the PRIMARY source of alkalinity and hardness in a river. Hardness gets into the groundwater and rivers when water percolates through rocks or deposits of limestone, chalk or gypsum, which are largely made up of calcium and magnesium carbonates, bicarbonates and sulfates.

IF the only source of hardness and alkalinity came from $CaCO_3$ (which is the predominant mineral in LIMESTONE, common in Colorado geology) then these two would be equal in concentration; hardness (Ca^{2+}) would equal alkalinity (CO_3^{2-}). In high mountain streams in Colorado, we generally see very low concentrations of alkalinity and hardness and the concentration of each is similar. The streams have little time to pick up (dissolve) hardness (cations) and alkalinity (anions) from rocks. As streams move downstream they have an opportunity to dissolve more of the cations and anions, so hardness AND alkalinity will increase.

Aquatic systems with hard water often have other elements like salts, suspended solids, nutrients, iron and/or sulfur. Harder water is often more biologically productive, has greater biomass and greater species diversity than soft water. These increases are a result of hardness, but also because of these other associations. Hard water can leave a crust or white film when it evaporates, (sometimes found around faucets), a yellow stain, smell, create a tannin color or have other effects – not all these affects are from the Ca^{2+} or Mg^{2+} present in water, but come from other elements prevalent in water. Soft water is less productive in terms of primary productivity, species diversity and total biomass.

Hardness is a widely used term, often confused by the use of water softeners. Hard water makes using soap difficult because it won’t lather. Water softeners make hard water functional or able to lather up and clean our bodies, clothes or cars. In general, water softeners work by replacing Ca^{2+} and Mg^{2+} with Na^{+} (sodium) K^{+} (potassium) ions. Soft water has a slimy feeling but does lather well.

There will always be some amount of hardness and alkalinity in any river because there is always some geology that water flows over/through to get to the surface. In regards to rivers, hardness cannot be too high but other elements often associated with hard water can be harmful to aquatic life and productivity at some point.

Chart 5 defines the Environmental Protection Agencies range for hardness levels.

Chart 5

Levels of Water Hardness mg/L $CaCO_3$ (Environmental Protection Agency 1976)

Soft	0-75
Moderate	75-150
Hard	150-300
Very Hard	300+

Hardness is measured in mg/L $CaCO_3$ (like alkalinity). Water does not contain X mg/L of $CaCO_3$, but behaves as if it does contain X mg/L of $CaCO_3$. Think of the Ca^{2+} part of the $CaCO_3$ equation as units of hardness. This unit provides a common language to compare hardness and alkalinity results across waterbodies. The River Watch hardness titration measures NOT ONLY the Ca (Calcium) half of Calcium Carbonate but also measures other cations that are present in the water, including Mg^{2+}. In headwater (high mountain) waters there is less opportunity to dissolve these cations, therefore these systems typically have low hardness numbers. As the stream flows downstream it interacts with more geology that not only has limestone but other rocks that add other cations to the mix. These are primarily Mg (Magnesium) and Fe (Iron) and others too, but to a much lesser extent. So hardness will increase as the stream moves downstream.

Therefore, a good general statement is that there are more cations contributing to the hardness number than just calcium from limestone. As rivers travel downstream, they become larger, deeper, and wider and both alkalinity and hardness increase. Why does hardness increase more than alkalinity? Since the alkalinity concentration is measuring one specific anion that comes from one primary source; that concentration will almost always be LESS than the hardness concentration which is coming from the calcium carbonate with the addition of other cations. The farther a stream moves downstream the greater the difference between these two concentrations increases.

Why do we care about hardness?

For aquatic life, hardness mitigates the toxicity from elevated levels of metals; hardness reduces the impact of harmful metals in water.

Ample documentation exists that demonstrates when fish reside in high hardness waters, they can withstand higher concentrations of metals compared to the same metal concentration in a low hardness environment. The hardness appears to "protect" fish from the effects of elevated metals. It is not known exactly how hardness mitigates toxic impacts from elevated metals. It is thought that the available Ca^{2+} and Mg^{2+} out compete the dissolved metals, such as Cd^{2+} or Fe^{2+} on the gill sites of fish. Gills are physically damaged and also functionally impaired in water with elevated metals. The more calcium and magnesium present, the better the odds of those ions being on the gill uptake sites than a harmful metal. Additionally, the presence of cations such as Ca^{2+} and Mg^{2+} physically repel other positively charged metals, such as Cd^{2+} or Fe^{2+}. Generally the dissolved ion, or free form of the metal harms aquatic life. Thus, hardness is inversely related to metal toxicity.

How do we measure hardness?

River Watch measures hardness with an acid based titration method, using EBT (Erichrome black T powder) and ammonia buffer as indicators. This is known as a complexation reaction. EBT binds to Mg^{2+} ions at high (basic) pH value. This EBT-Mg^{2+} complex is magenta. We then slowly titrate the sample from magenta to blue using EDTA (ethylene diamine tetra acetic acid). The first drop of EDTA added that maintains a blue color in your sample is equivalent to the concentration of multivalent cations present in solution – the hardness.

How does this work? Initially we add 15 drops of ammonia buffer to our river water sample. This raises the pH of the sample above 10 and holds it at that pH (buffers the sample; **remember** a buffer is something that will resist a change in pH). Ammonia buffer will not change the color of your sample, however, if you were to measure the pH change, you would see it rise rapidly to above 10. Next we add a small amount of the EBT powder to the solution and swirl, at this elevated pH, the EBT binds all of the Mg^{2+} present in solution and this complex is magenta. If you add in the EBT before the ammonia buffer, you can make the sample turn purple. However, when you add the ammonia buffer, the sample will be too dark to titrate. Your sample can be too light (not enough EBT) or too dark (too much EBT), which may cause you to underestimate or overestimate the hardness. The goal is a consistent density magenta that you could 'read" words through if you set the flask on your instructions.

Then, after zeroing the burette, we slowly add EDTA to the solution. EDTA is a chelator, a chemical term meaning it binds metals. EDTA is one of the BEST chelators out there and has effectively 6 teeth to envelop metals. At this point EDTA begins to envelop multivalent metals present in solution, most of these are Mg^{2+} and Ca^{2+}, but EDTA also binds Pb, Zn, Cu, Mn etc. (just remember these are FAR less abundant than Mg and Ca). Initially, EDTA chooses Ca over Mg because the Mg is bound up with EBT (causing your solution to be magenta) so the EDTA, drop by drop, begins to bind to calcium until all the calcium is bound, still you will see no color change, your solution will remain magenta. Once the Ca has been consumed, the EDTA, starts to outcompete EBT for Mg, stealing Mg from the EBT-Mg complex. This is where you slowly see the color change from magenta to purple. Drop by drop EDTA is added until all the Mg is bound up. At this point the solution turns blue. If you continue to add EDTA, the color will remain blue, as there are no more metals cations to bind in solution. For this reason, the last drop of EDTA added that maintains a blue color is your endpoint and equivalent to the hardness is solution.

Chemical reactions:

[EBT + ammonia buffer] = (blue) + Mg^{2+} ⇔ MgEBT (magenta)

EDTA + Ca^{2+} ⇨ CaEDTA

EDTA + Mg^{2+} ⇨ MgEDTA

EDTA + MgEBT (magenta)   MgEDTA + EBT (blue)

What Influences Hardness?

Watershed geology

Variations in hardness can be attributed to the substrate and soils the water runs over and through. More limestone yields higher hardness than silica rock. On a side note, this is also why alkalinity and hardness typically increase during low flow months. The primary source of these constituents are geology and groundwater (these remain relatively constant over the course of a year). When river flows increase (spring runoff), these concentrations are diluted by runoff. This is also why we see a seasonal fluctuation in metals concentration (lower during runoff). Despite lower metal concentrations that can occur during spring runoff, when hardness also is diluted, the protection offered to aquatic life from hardness is reduced. For these reasons aquatic life are more threatened by metals in the spring high flow months than at other times of the year when hardness offers better protection.

Climate and precipitation

Wetter and warmer climates have different soil types and vegetation. Likewise, hardness will vary depending on precipitation. Typically high water flows in Colorado result in lower hardness due to dilution.

Land use activities

Land use activities that disturb enough soil that makes its way to the surface or groundwater can increase hardness concentrations. Some examples include water applied to land. Flood irrigation can artificially increase hardness in waterways through irrigation return flows for example. Certain industrial processes could also increase hardness. When groundwater is pumped to the surface for agricultural or industrial needs and later reaches the stream, it may increase the hardness. Finally construction activities in or near streams can disturb soil causing increased hardness concentrations.

How does hardness fluctuate?

- **Daily** – hardness does not fluctuate much; it is difficult to measure if it does, because sources do not change daily
- **Seasonally** – typically hardness is lower during runoff due to dilution, and higher in low flow
- **River, Lake/Reservoir, Groundwater Concentrations** – rivers will generally have the lowest values, next higher is lakes and reservoirs and groundwater will depend if it is calcium carbonate dominated geology or sodium and potassium dominated geology.
- **River Continuum** – High in the mountains, alkalinity and hardness are typically low and can be close in concentration. As you move down in a watershed both alkalinity and hardness INCREASE, though typically hardness increases more rapidly than alkalinity.

A deeper dive:

Why does hardness increase more than alkalinity as you move downstream? One reason is that alkalinity can be consumed in solution (i.e. utilized to assist with buffering in the presence of an acid or a base for example). Generally Mg, and Ca (simplified, this is hardness) are conserved. Furthermore, since the alkalinity concentration is measuring one specific anion (HCO_3^- or CO_3^{2-} depending on the pH) that comes from one primary source (geology), that concentration will almost always be LESS than the hardness concentration which is coming from the calcium carbonate with the addition of other cations. The farther a stream moves downstream the greater the difference between these two concentrations increases.

WHY? HOW do they buffer/mitigate metal toxicity?
Hardness and alkalinity “BUFFER” a stream from insults (toxicity) caused by dissolved (free radical) metals concentrations. To account for this many metals standards in Colorado are calculated using the HARDNESS concentration. The higher the hardness, the more metals a stream can contain before they become toxic.

What is the relationship between hardness and alkalinity concentrations and the metals standards? First and foremost, hardness and alkalinity concentrations INCREASE as you travel downstream. Second, hardness and alkalinity "BUFFER" a stream from insults (toxicity) caused by dissolved (free radical) metals concentrations. Third, metals concentration standards are calculated using the HARDNESS concentration. The higher the hardness, the more metals a stream can contain before they become toxic.

Metals, in their dissolved state, are either absorbed through the gills or ingested by aquatic organisms through their gills and through ingestion. Many of these metals are then concentrated in the organism and at some point will become toxic (ex. Mercury, selenium).

Alkalinity (anions, negative charged ions HCO_3^- and CO_3^{2-}) buffers or mitigates toxicity by **BINDING** with free radicals (cations, positively charged elements, Cd^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+} etc.) that is the dissolved metal. This takes the metal from its "toxic" state to a bonded state that is no longer reactive and is now non-toxic. These often precipitate (fall out) of solution and are deposited in the sediment where they are less bioavailable to aquatic life.

Hardness (the cation, positive charge, Ca^{2+}, Mg^{2+}) buffers or mitigates toxicity by **COMPETITION**. An aquatic organism will naturally pick up "X" amount of these cations from its environment. These cations can be loosely divided into the "good guys" (hardness cations) and the "bad guys" (metals). The "good guy" to "bad guy" ratio in a headwater high-mountain stream is very low (low hardness, potentially high metals), therefore the organism will tend to pick up more "bad guys." As you move downstream the stream picks up more and more "good guys" while the "bad guys" remain relatively constant or increase very little.

A headwater (high mountain) stream near a town like Fairplay will have very low hardness and alkalinity and therefore have very little capacity to "BUFFER" against insults from even very low metals concentrations. A river near Sterling will have extremely high hardness and alkalinity and therefore can "BUFFER" against a fairly high metal concentration.