Chemical Properties of Water

Water is never absolutely pure in nature. There are always various substances dissolved that come from the soil or rocks (through leaching), the air and the metabolism of several aqatic and semi-aquatic organisms. Even rain drops contains very small amounts of nutrients, they may also get saturated with atmospheric gases. In fact, many substances dissolve in water that it is sometimes referred to as the "Universal Solvent." While most of these substances are important for healthy aquatic ecosystems, as concentrations increase, they can have negative effects (many of those toxic substances are so called pollutants).

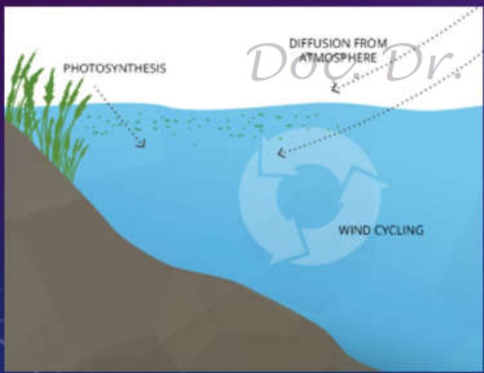
Parameter	Maximum	Minimum	Mean[#]
pH	8.8	7	7.7
Phenolphthalein alkalinity	19	0	8.9
Total alkalinity	317.3	218.5	266.5
Total hardness	226.2	116.7	182.4
Chloride	266	44.2	137.5
Chemical oxygen demand	294.6	16.3	62.2
PO_4	3.5	0.1	1.3
SO_4	2167.1	299.4	752.1
Ca	153.8	52.3	80.6
Mg	38.8	5.8	24.8
Na	88.49	28.51	58.8
K	97.1	3.5	53.9
Fe	11.89	0.54	3.9
Mn	0.17	0.02	0.08
Cr	0.02	ND	0.02
Cu	0.02	ND	0.01
Ni	0.04	ND	0.02
Pb	0.08	ND	0.04
Zn	0.2	ND	0.11

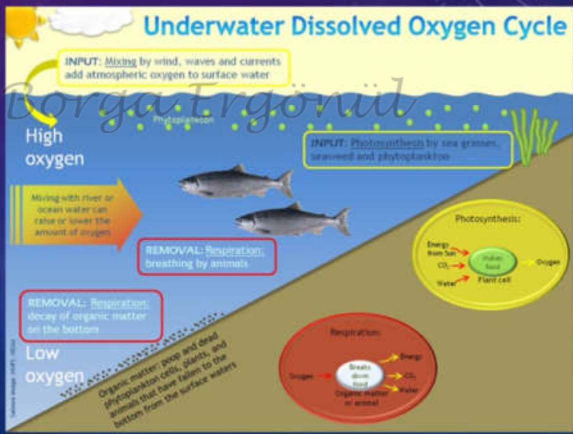
* All concentrations except for pH are in milligrams per liter. ND = not detectable.

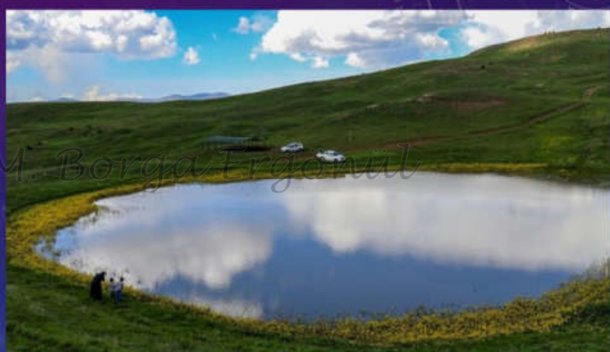
[#] samples were analyzed in triplicate.

Dissolved oxygen

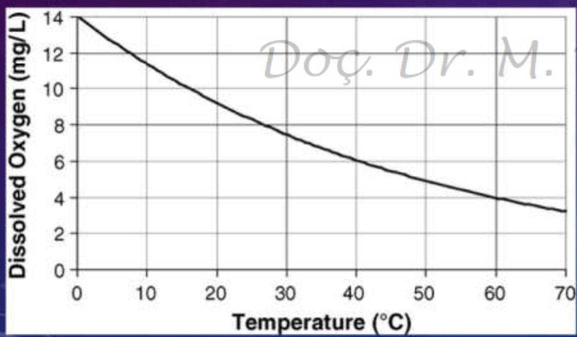
Dissolved oxygen (DO) is one of the most important constituents of water and refers to the amount of oxygen that is present in water. Water bodies receive oxygen from the atmosphere and from aquatic plants (through photosynthesis). Running waters, such as that of a swift moving stream, dissolves more oxygen than the still water of a pond or lake. Waves, rapids and tumbling over falls increase the surface area of water that get in contact with atmosphere.







Under normal conditions at 1 atm pressure at 0°C the maximum solubility of oxygen in water is 14,63 mg/L but if the temperature rise up to 30°C oxygen solubility decreases to 7,57 mg/L. Thus there is a negative correlation between the solubility of oxygen and temperature of water. On the other hand, the salinity of the water has also an effect on the oxygen concentration in water.

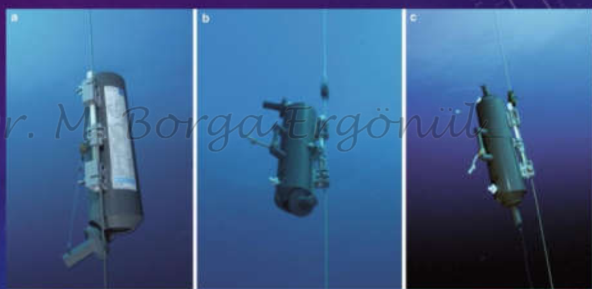


Sıcaklık	Tatlısu	‰ 35'lik deniz suyu
0 c°	10.3 ml/l	8.0 ml/l
10 c°	8.0 ml/l	6.4 ml/l
20 C°	6.6 ml/l	5.3 ml/l
30 C°	5.6 ml/l	4.5 ml/l

How do we measure DO?

Multiparameter device probes

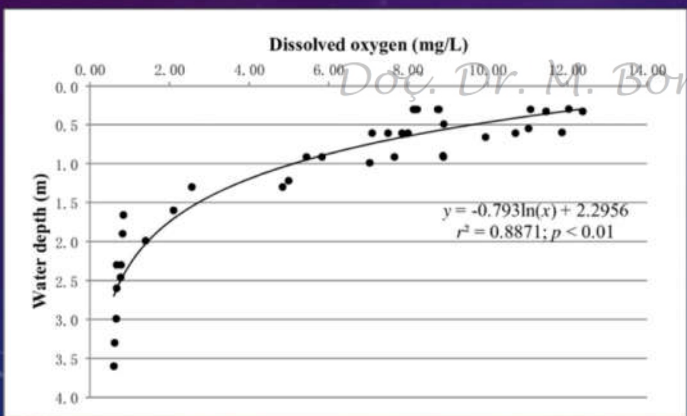
What about deeper parts of a water body?



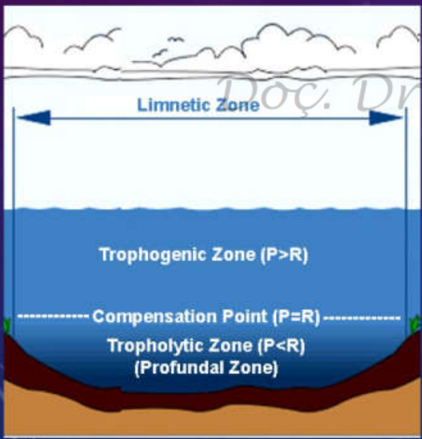
Niskin bottle

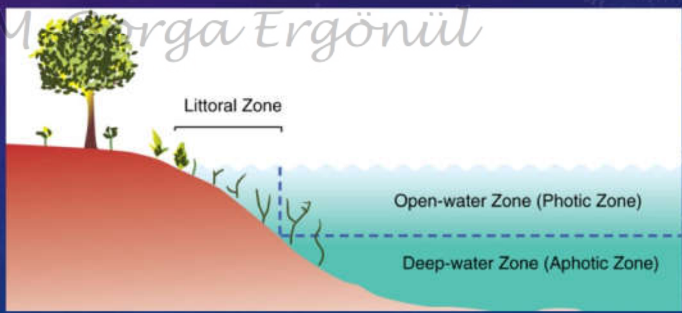
Nansen bottle (developed by Fridtjof Nansen in 1894)

In lakes the amount of DO changes depending on the depth. Generally (**but not always**) the DO levels decrease when you go deeper due to light availability (thus photosynthesis) and respiration rates (high oxygen consumption rate due to decomposition of organic materials).



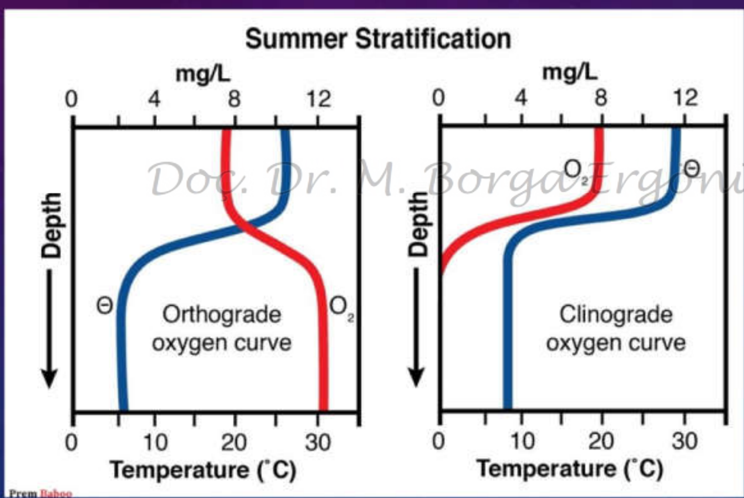
The photosynthetic organisms (also called primary producers) are only found in the zones where light is present. This the upper portion of the lake where photosynthesis occurs is called the trophogenic zone (also called euphotic-photic zone). In this zone the production of biochemical energy through photosynthesis is greater than its consumption through respiration and decomposition. Do not forget that animals and decomposers are found in both the photic and aphotic zones. In the aphotic zone, also called the tropholytic zone, where light availability is reduced, the consumption rate of oxygen exceeds its production.





Depending on the depth, two distinct types of oxygen profiles are observed in lakes (eutrophic vs oligotrophic) during summer stratification.

Oligotrophic lakes



Eutropic lakes

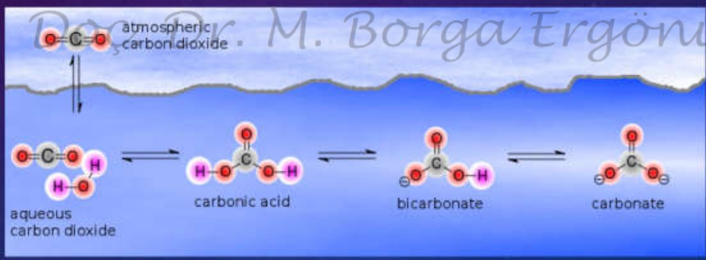
During spring turnover the whole lake reaches to a fully oxygen-saturated status (around 12 mg/L) both in eutrophic and oligotrophic lakes

In oligotrophic (unproductive) lakes, oxygen concentration with depth is regulated physically means mainly by seasonal changes in temperature. As temperature increases in the epilimnion, oxygen concentration decreases. If stratification is maintained (e.g. summer stratification), the oxygen content in the hypolimnion will be higher than of the epilimnion because saturated cold water from spring turnover is exposed to a limited oxidative consumption. In oligotrophic lakes the low nutrient status implies that the overall productivity is low. Thus oxygen consuming processes (mainly decomposition) in the hypolimnion is low and hence high oxygen saturation. This type of oxygen profile is known as orthograde oxygen profile and largely regulated by physical processes.

Clinograde oxygen profile can only be found in eutrophic (high nutrient inputs thus highly productive) lakes. High nutrient status leads to a high organic production which settles in the bottom layers. Biological oxidation of organic matter in the sediment leads to depletion of oxygen. During summer stratification, the bottom layers (hypolymnion) of eutrophic lakes remains anaerobic. Here, oxygen concentration at the epilimnion will be higher than that at the hypolimnion. This type of oxygen profile termed as clinograde oxygen profile. Clinograde oxygen profile is largely regulated by biological processes.

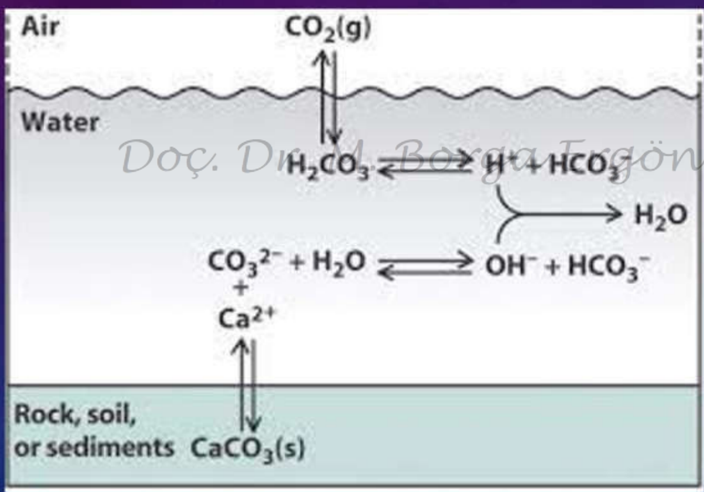
Carbon dioxide in waters

The carbon is used by several primary producers as the primary element in organic material synthesis. The primary source of CO2 in aquatic habitats is the atmopshere. The current concentration is about 0.04% (412 ppm) by volume. Carbon dioxide is found in water as a dissolved gas. It can dissolve in water 200 times more easily than oxygen. Thus, the gas CO_2 is quite soluble in water in which more than 99% exists as the dissolved gas and less than 1% as carbonic acid H_2CO_3, which partly dissociates to give H^+, HCO_3^-, and CO_3^{2-}. These ions can be used by plants as a source of organic carbon for photosynthesis.



When carbon dioxide reacts with water a weak acid (carbonic acid) is formed. Carbonic acid plays a major role on the pH of aquatic environment.

The pH in a water body is determined by the relation between CO2 and carbonate or more precisely by the H+ ions arising from the dissociation of H2CO3 and the OH- ions arising from the hydrolysis of bicarbonate.

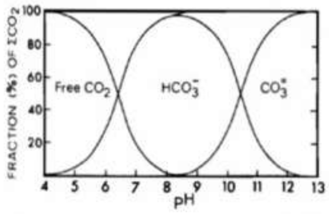


The bicarbonate (also called carbonate system) buffer system is an acid-base mechanism involving the balance of carbonic acid (H2CO3), bicarbonate ion (HCO−3), and carbon dioxide (CO2) in order to maintain pH in aqueous systems (also in blood). The carbonate system is very important since it regulates the pH of sea water, and but also controls the circulation of CO2 between the biosphere, the lithosphere, the atmosphere and the oceans and lakes.

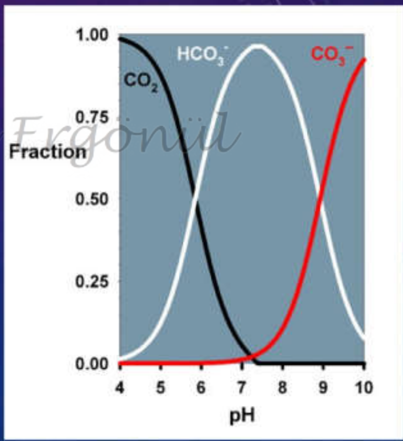
The bicarbonate buffer system

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

pH



- **Determines the predominant form of DIC in freshwater systems.**



pH

pH is a measure of the hydrogen ion concentration of the water as ranked on a scale of 1.0 to 14.0. The lower the pH of water, the more acidic it is. The higher the pH of water, the more basic, or alkaline, it is. pH affects many chemical and biological processes in the water and different organisms have different ranges of pH within which they flourish. The largest variety of aquatic animals prefer a pH range of 6.5 - 8.0. pH outside of this range reduces the diversity in water bodies because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds such as heavy metals to become mobile and "available" for uptake by aquatic plants and animals. Since the scale is logarithmic, a drop in the pH by 1.0 unit is a 10-fold increase in acidity. So, a water sample with a pH of 5.0 is ten times as acidic as one with a pH of 6.0. pH 4.0 is 100 times as acidic as pH 6.0.

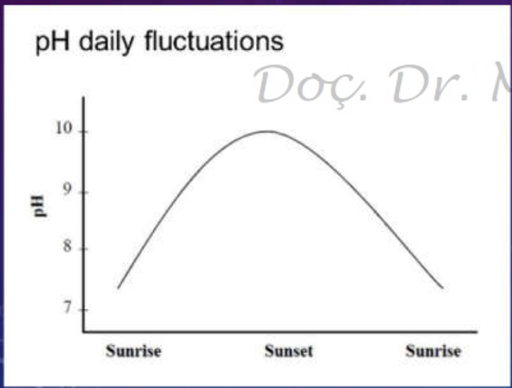
pH

The p means the negative log has been taken.

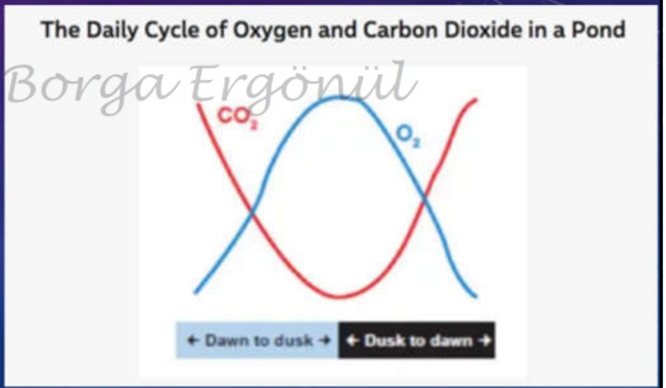
The letter here tells what ion's concentration is being described. H stands for H^+

Water characteristics	pH
Waters of volcanic exhalation	>2
Mine waters	3-4
Swamps	4-6
Groundwaters	5-7
Rivers	6.8-7.8
Fresh lakes	7.3-9.2
Ocean	7.8-8.3
Salt (soda) lakes	up to 10.5

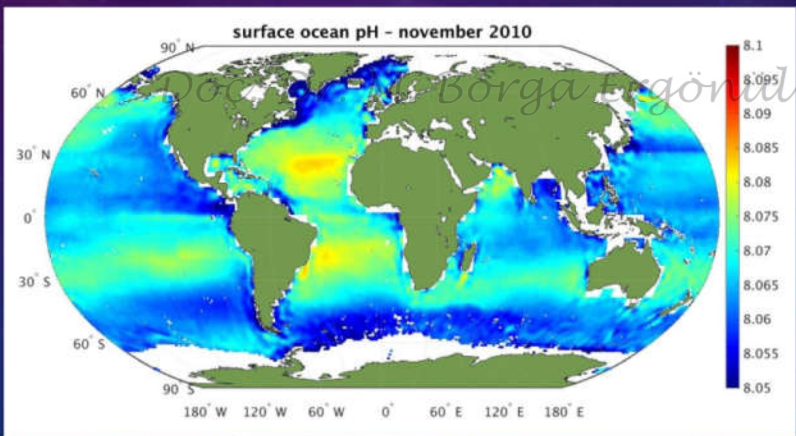
During the dark stage of photosynthesis, organic compounds are formed by using carbon dioxide as a carbon source. As the CO2 decreases the pH will increase As photosynthesis rates increase the amount of O2 produced will also increase.



In highly algae dominated lakes.

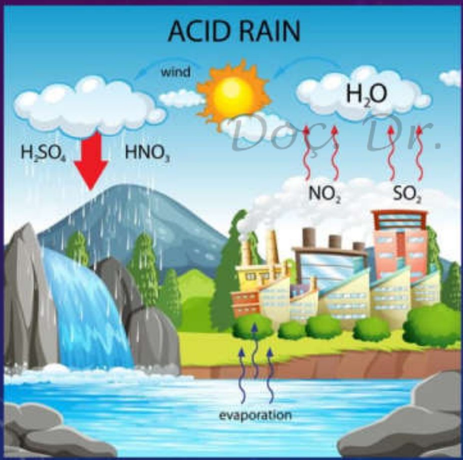


The pH of marine waters is close to 8.2, whereas most natural freshwaters have pH values in the range from 6.5 to 8.0. The oceans generally have a higher alkalinity due to carbonate content and thus have a greater ability to buffer free hydrogen ions. Most waters have some capacity to resist pH change through the effects of the carbonate-buffer system. Generally



A paranthesis here: Acid Rains

Acid rain is a rain or any other form of precipitation that is unusually acidic, meaning that it has elevated levels of hydrogen ions (low pH). It can have harmful effects on plants, aquatic animals, and man made structures. Acid rain is caused by emissions of sulphur dioxide and nitrogen oxide, which react with the water molecules in the atmosphere to produce acids.



Chemical Processes Involved In acid rain

Formation Of Sulphuric Acid

$$S + O_2 \longrightarrow SO_2$$

$$SO_2 + 1/2O_2 + H_2O \longrightarrow H_2SO_4$$

Reaction Involving Formation Of Nitric Acid

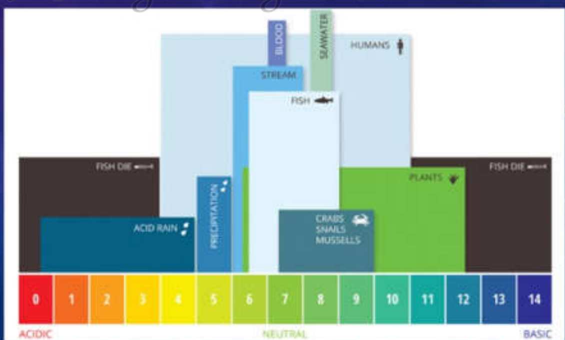
$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

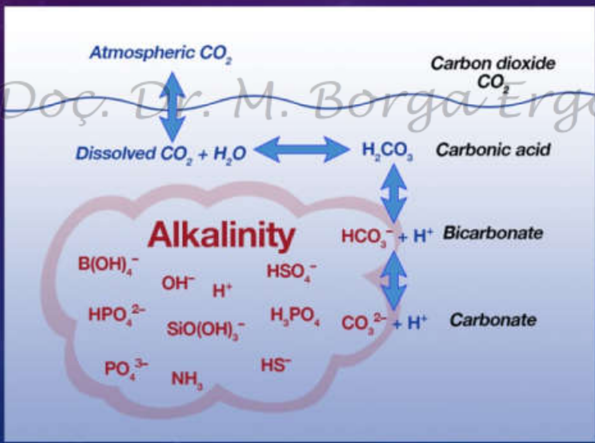
$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

The ecological effects of acid rain are most clearly seen in aquatic environments, such as streams, lakes, and marshes where it can be harmful to fish and other wildlife. As it flows through the soil, acidic rain water can leach several heavy metals such as aluminum from soil clay particles or bed rock and then flow into streams and lakes. The more acid that is introduced to the ecosystem, the more metal is released. Some types of plants and animals are able to tolerate acidic waters. Others, however, are acid-sensitive and will be lost as the pH declines. Generally, the young or larvae of most species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, most of the adult fish die. Even if a species of fish or animal can tolerate moderately acidic water, the animals or plants it eats might not. For example, frogs have a critical pH around 4, but the mayflies they eat are more sensitive and may not survive pH below 5.5.

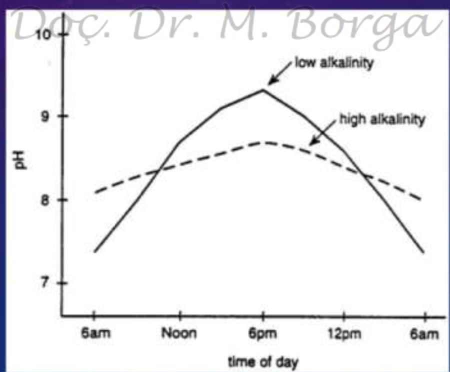


Alkalinity

Water alkalinity and pH are not the same. Water pH measures the amount of hydrogen (acid ions) in the water, whereas water alkalinity is a measure of the carbonate and bicarbonate levels in water. In other words alkalinity is the buffering capacity of a water body. It measures the ability of water bodies to neutralize acids and bases thereby maintaining a fairly stable pH. Water that is a good buffer contains compounds, such as bicarbonates, carbonates, and hydroxides, which combine with H+ ions from the water thereby raising the pH (more basic) of the water. Borates, silicates, and phosphates also may contribute to alkalinity. But they are usually neglected.



A base is a substance that releases hydroxyl ions (OH^-) when dissolved in water. In most waters these bases are principally bicarbonate (HCO_3) ions and carbonate ions (CO_3^{2-}). These ions are the buffers in water; that is they buffer the water against sudden changes in pH. High alkalinity means that the water body has the ability to neutralize acidic pollution from rainfall or basic inputs from wastewater. Alkalinity refers to the total amount of bases in water expressed in mg/l of equivalent calcium carbonate. Waters of low alkalinity (<20 mg/l) are poorly buffered, and the removal of carbon dioxide (CO_2) during photosynthesis results in rapidly rising pH. Waters, with greater than 20 mg/l alkalinity have greater buffering capacity and prevent large fluctuations in pH during photosynthesis.



Doç. Dr. M. Borga Ergönül

Hardness

Alkalinity and hardness are generally similar. As we allready mentioned that alkalinity is an index of the capacity of water to neutralize acidity (usually expressed in mg/L of equivalent calcium carbonate).

Hardness is most commonly associated with the ability of water to precipitate soap. As hardness increases, more soap is needed to achieve the same level of cleaning due to the interactions of the hardness ions with the soap. In a chemical way; hardness is often defined as the sum of polyvalent cation concentrations dissolved in the water. The most common polyvalent cations in fresh water are calcium (Ca^{++}) and magnesium (Mg^{++}). Thus, hardness is the concentration of metal ions (primarily calcium and magnesium) expressed usually in the same way as alkalinty. Hardness can be referrred as Calcium hardness or Total hardness (Sr, Mn, or sometimes resulting from Fe) both indicating different measurements.

There are 2 types of hardness in waters: temporary and permanent hardness. Temporary hardness results from the carbonates of Ca and Mg where permanent hardness results from the nitrates, sulphates and chlorides of Ca and Mg. Temporary hardness can be removed by boiling the water.

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Calcium Carbonate}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$\underset{\text{Magnesium Bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Magnesium hydroxide}}{Mg(OH)_2\downarrow} + 2CO_2\uparrow$$

– Calcium/Magnesium Carbonates thus formed being almost insoluble, are deposited as a scale at the bottom of vessel, while carbon dioxide escapes out.

Temporary Hardness	Permanent Hardness
Temporary hardness is due to the presence of bi-carbonates of calcium and magnesium.	It is due to the presence of chlorides of Sulfates of Calcium and Magnesium.
Can be removing by boiling.	Can't be removing by boiling.
Hardness removal is cheap.	Hardness removal is expensive

Conversion for the units of the water hardness

		°gH	°e	°fH	ppm	mval/l	mmol/l
German grade	1 °dH =	1	1,253	1,78	17,8	0,357	0,1783
English grade	1 °e =	0,798	1	1,43	14,3	0,285	0,142
French grade	1 °fH =	0,560	0,702	1	10	0,2	0,1
ppm $CaCO_3$ (USA)	1 ppm =	0,056	0,07	0,1	1	0,02	0,01
mval/l Earth alkali ions	1 mval/l =	2,8	3,51	5	50	1	0,50
mmol/l Earth alkali ions	1 mmol/l =	5,6	7,02	10,00	100,0	2,00	1