Hydrology 101a

Dissolved Solids, Conductivity, and Hardness

Objectives: To introduce the concept of concentration, and to measure the concentration of dissolved solids and hardness in water. To learn the use of the conductivity meter, and to develop a simple relation between conductivity and the concentration of dissolved solids. To learn the difference between dissolved solids, conductivity, and hardness.

Background: Natural water is never completely pure. The purest spring water probably contains a few hundred milligrams of dissolved minerals per liter, and the drinking water of some cities, like New Orleans at the mouth of the Mississippi River, often contains very high concentrations of dissolved species, including man-made pollutants.

Water, because it is a polar molecule, makes a very good solvent for other polar molecules, and many salts dissolve easily in it. The atoms that make up the minerals found in the rocks of the earth's crust are locked in a crystal structure. Most are held in place by ionic bonds. But when water passes over the rock, some of the bonds break. Electrically charged atoms, called ions, are surrounded by water molecules, and we say that the water dissolves the rock (see Figure 1A).

The ions are very tiny particles, with diameters on the order of angstroms (10^{-10} meters), and they carry positive or negative charges. A water molecule has a size of 2.5 angstroms. When water dissolves minerals, the minerals no longer have their original identities. The mineral is dissolved or broken down into tiny ions. The sodium ions (Na^{+}) and chloride ions (Cl^{-}) in a river may just as easily come from granite as from a salt deposit (NaCl). Of course, the chemical composition of water depends on the rock over which the water flows, or the pollutants that people put into it. Water flowing through limestone ($CaCO_3$) will be high in calcium ions (Ca^{2+}) and water flowing past a city will likely increase in nitrate (NO^{-3}) ion concentration due to sewage discharges or urban runoff. It is important to know how much dissolved material is in water because if there are a lot of dissolved minerals, water may taste undesirable or may not be fit for use agriculturally.

How do we measure the amount of ions in water?

There are many ways to measure the amount of ions in water. To make a measurement of the total amount of ions in a solution, the Total Dissolved Solids (TDS) or the Conductance can be measured. A hardness test is used to measure the specific ions that cause "hardness" of water.

First, it is important to understand the concept of concentration.

Concentration:

The quantity of dissolved species is expressed in terms of **concentration**. The substance that is dissolved is called a solute. The substance that does the dissolving is called the solvent, and the mixture of solute and solvent is called a solution. For example, water is a solvent, salt is a solute, and salty water is a solution. **Concentration is the amount of solute in a given amount of solution.**

The "amount" can be expressed in many ways. The units used depends on the context in which the data is to be used. One of the most common ways to express concentration is as a **mass of solute divided by volume of solution**. The units are then milligrams per liter (mg/L), or pounds per cubic foot (lb/ft^3), or tons per acre-foot (tons/acre · ft), etc.

Another way to express concentration is as **mass of solute divided by the mass of solution.** The most common units here are parts per million (ppm). For dilute water solutions, where the major weight component is water, ppm is identical to mg/L. This is because here are 10^6 mg in a liter of water.

Another way to express concentration is as **weight percent (wt %)**:

$$\text{wt \%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100 \qquad (1)$$

This is very similar to expressing concentration as parts per million (it is actually parts per hundred), but ppm is more suitable for very dilute solutions such as are normally found in nature.

Finally, another common way of expressing concentration is as **moles per liter** (moles/L). A "mole" is a large number (called Avogadro's number) and is equal to 6.022×10^{23}. The atomic weights given in the periodic chart of the elements are the number of grams in a mole of atoms of an element. The way to determine the number of moles you have is to divide the mass that you have by the molecular weight. Thus, in chemical problems it is often very convenient to use moles/L to describe concentrations, where you divide the number of moles by the number of liters of solution. This concentration is called the **molar concentration**.

Dissolved Solids: As mentioned above, as water passes over rocks, it dissolves minerals in the rocks. The solid minerals are pulled apart by attraction from the water molecules, forming ions. The ions are surrounded by water molecules so they cannot recombine (See Figure 1A). However, when water is evaporated, the ions will recombine to form solids. This is what happens when a bucket of sea water (salt water) is left in the sun. The pure water evaporates, allowing the sodium and chloride ions to recombine to form a salty, solid crust on the edges of the bucket.

Likewise, if given a sample of water, the amount of Total Dissolved Solids (TDS) can be measured and calculated it as follows:

1) Weigh an empty porcelain dish and record its weight. This is called the **tare weight.**
2) Pass a known volume of water thru a filter, catching the water in a flask. The filter or filter paper will trap the solid materials but allow the dissolved solids (ions) to pass through with the water. The water that passes thru the filter and into the flask is called **filtrate.**
3) Pour the filtrate into the pre-weighed porcelain dish.
4) Place the dish with the water in it into an oven at 180°C for at least 1 hour to drive off all free and chemically bound water. A dry residue (crust) will be left in the dish.
5) Weigh the dish + residue.
6) Subtract the weigh of the dish from the weight of the dish + residue to obtain the weight of the residue alone.

7) Divide the weight of the residue by the volume of water originally used to filter (g/ml).

8) Convert to mg/L to obtain the concentration of dissolved solids (TDS).

$$\left(\frac{gm}{ml}\right)\left(\frac{1000ml}{1L}\right)\left(\frac{1000mg}{1gm}\right) = \left[\frac{mg}{L}\right]$$

Example:

A 50 ml sample was filtered. The tare weight of the dish was 36.012 grams. The dry weight of the dish + residue was 36.047 grams. What is the total dissolved solids concentration in mg/L?

Dry Weight of dish + residue	36.047 g
Tare Weight of dish alone	- 36.012 g
Weight of Residue (Dissolved Solids)	0.035 g.

$$\left(\frac{0.035g}{50ml}\right)\left(\frac{1000ml}{1L}\right)\left(\frac{1000mg}{1g}\right) = 700\ \frac{mg}{L}\ TDS$$

Conductivity: Water that has no dissolved ions does not conduct electrical current very well. It is a better insulator than a conductor. But add some positive and negative ions by dissolving salts in the water, and the water begins to conduct current. The more dissolved salts, the better conductor the water becomes. This property of conducting current makes it possible to estimate the concentration of dissolved species in the water, using a conductivity meter. (See Figure 1B and Figure 1C).

If we assume that all of the dissolved material in water adds to the conductivity of the water in the same way, then the conductivity meter can be used to measure the so-called total dissolved solids (TDS). Actually, this is not a correct assumption. But in many cases, the measurement of conductivity gives a good estimate of TDS. It is much simpler and faster to measure conductivity to obtain an estimate of the dissolved solids rather than waiting for water molecules to evaporate.

Conductivity is not expressed as a concentration, however. Conductivity is usually expressed in units of mhos/cm. A mho is the inverse of the unit for resistance, the ohm. A mho is a fairly large quantity, and in water analysis, the micromho is used (μmho). 1 μmho = 10^{-6} mho. Sometimes, the SI unit of siemens(S) is used. 1 μS/cm = 10 μmhos/cm. The unit of conductivity used depends on the equipment used. A probe can be used to dip into the water or the water can be poured into a measuring conductance meter.

Figure 1A

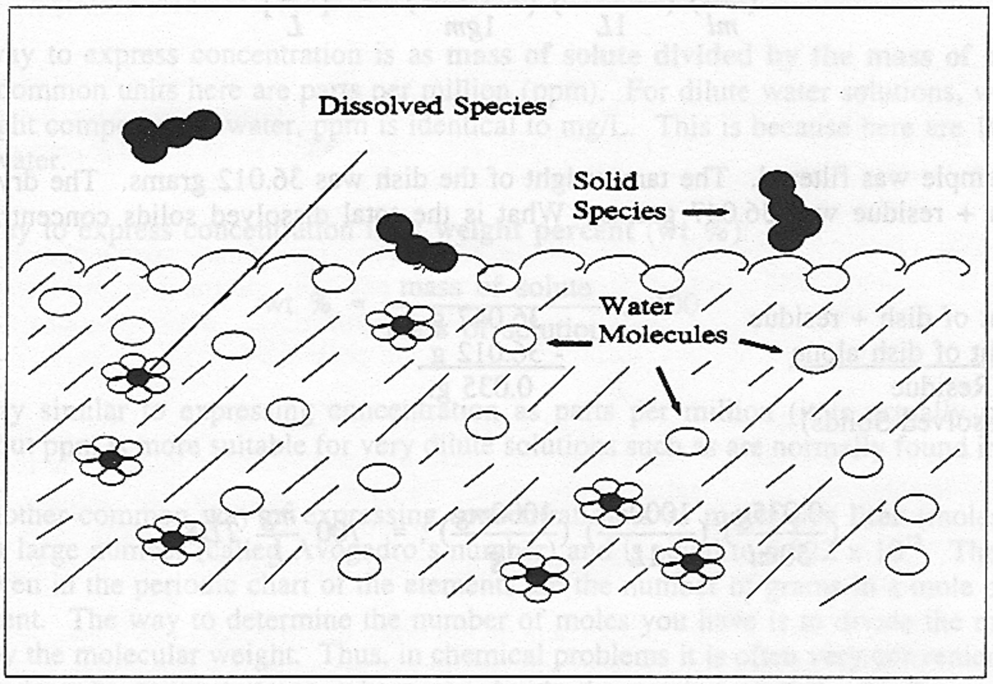

Figure 1B

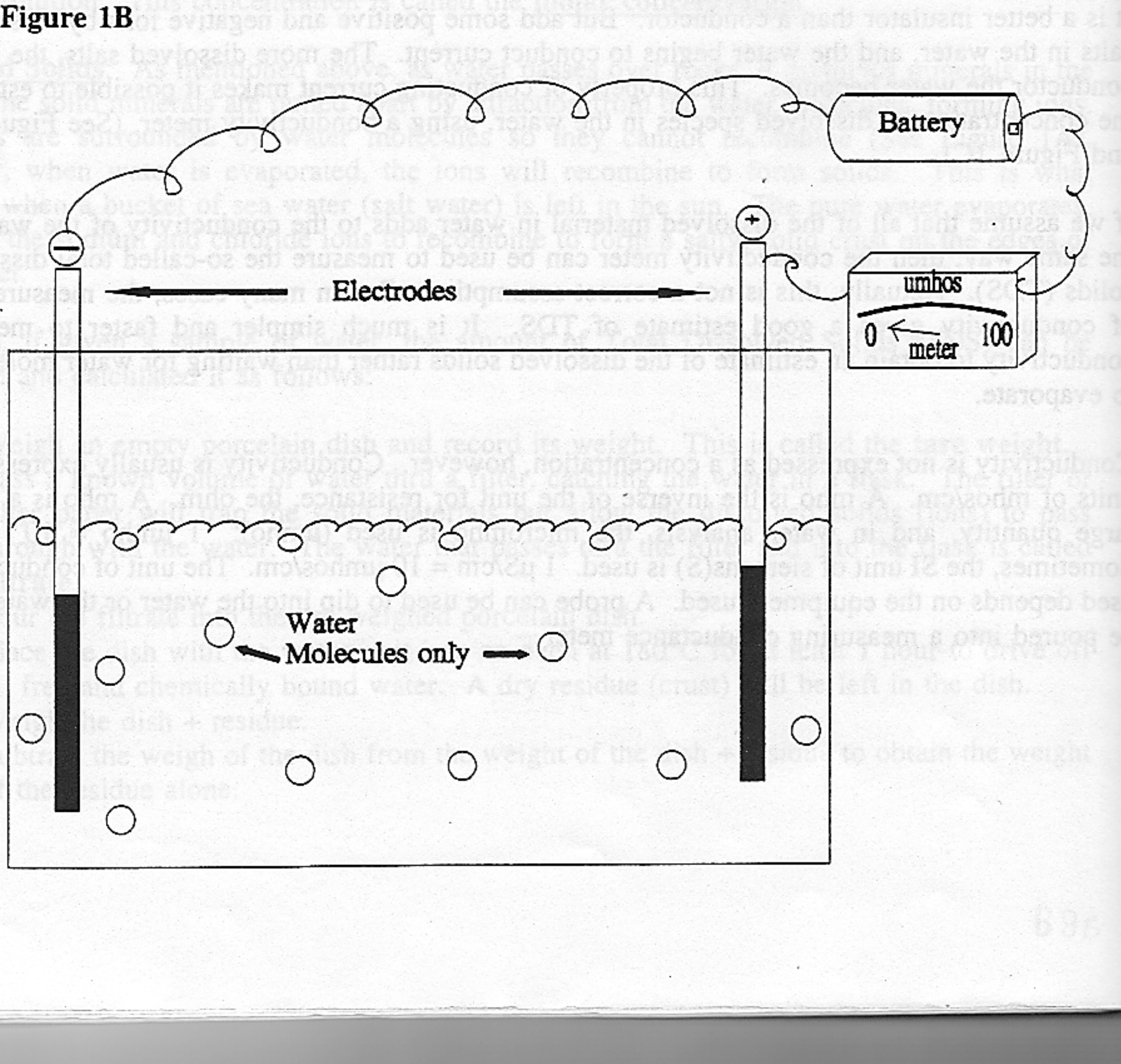

Figure 1C

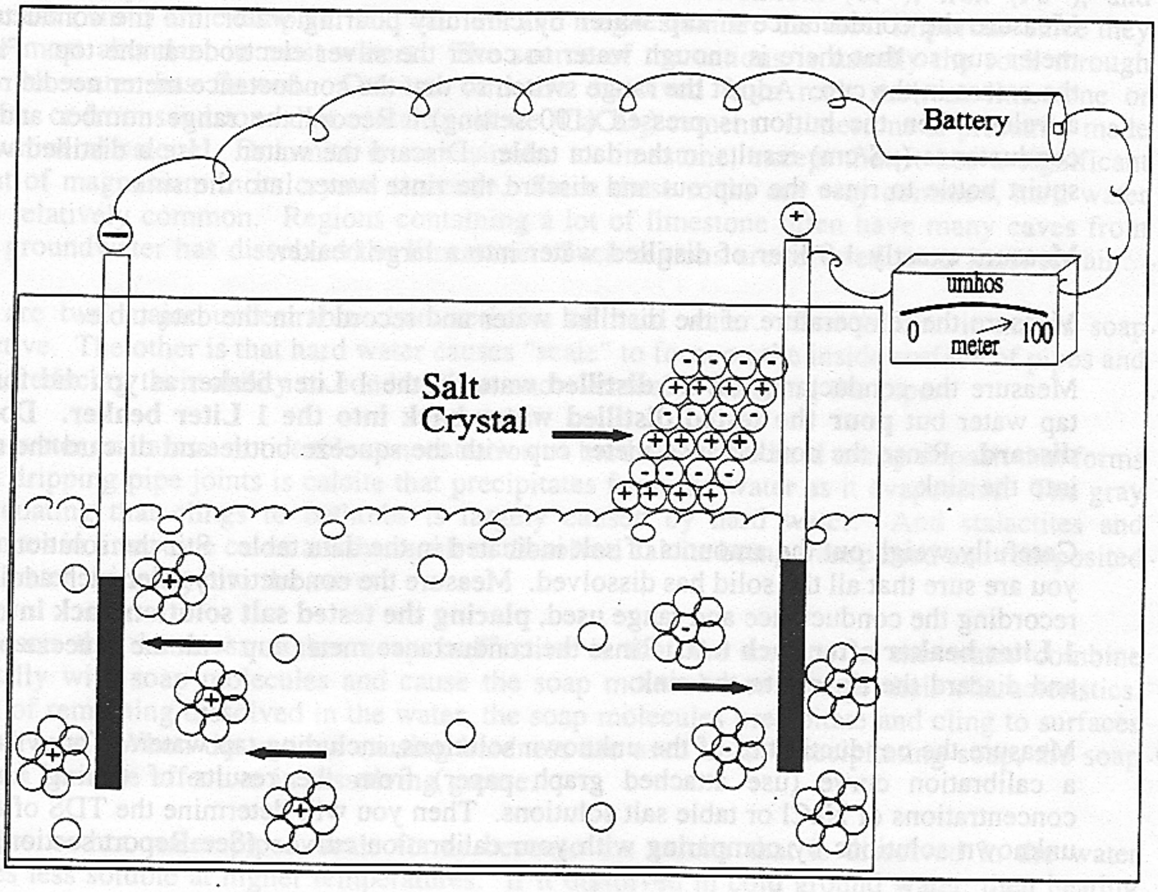

Figure 1A. The solution process: When a solid species such as salt is added to water it is pulled apart by attractions from the water molecules, forming ions. The ions are surrounded by water molecules and cannot recombine.

Figure 1B. The conductivity meter works by measuring a voltage between a positive and negative electrode in the probe. With only a solution of water, there is no movement of charges in the solution between the electrodes.

Figure 1C. When salt, or another ionic species, is added to the water, the positive and negative ions migrate to the oppositely charged electrode. With more ions in solution, the charge increases and the meter on the conductivity meter is deflected further to the right.

Summary: Testing for dissolved solids and conductivity can be used to obtain the total amount of dissolved or ionized species in the water, regarding each ion, no matter what type, as a part of the total measurement. TDS and conductivity include both positively and negatively charged ions (cations and anions) such as chloride (Cl^{-1}), sodium (Na^{+1}), fluoride (F^{-1}), as well as ions that cause hardness such as calcium (Ca^{+2}) and other metals with a $^{+2}$ charge. Hardness, on the other hand, measures only the ions that have a $^{+}2$ charge (Ca^{+2}, Mg^{+2}, Fe^{+2}, Sr^{+2}, and Mn^{+2}) because by definition, these are the ions that cause water "hardness".