Turf Irrigation Water Quality: A Reference Guide

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This guide is designed to familiarize people with water quality language and instrumentation. First, the language is presented in three subsections: the terms, units and equations of water quality. Second, the instrumentation is presented as seven basic laboratory techniques: spectrophotometry, atomic spectrometry, chromatography, titration, potentiometry, gravimetry and field. Finally, a list of references and an index of terms are located at the end of the guide.

The Language of Water Quality

This language is basically the same as used in freshman chemistry, except water quality practitioners have added some specialized terms, units and equations.

Terms

Anions are negatively charged ($^-$) ions. Monovalent anions, such as Cl^-, have one charge, while divalent anions, such as SO_4^{2-}, have two charges. Anions can also be polyvalent.

Cations are positively charged ($^+$) ions. Cations can also be monovalent (Na^+), divalent (Ca^{2+}) or polyvalent.

Base cations are four in all: calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+).

Anion-cation balances calculate whether the measured charges of anions and cations are equal in a water sample. If all of the ions in the water are measured, then the anions and cations should balance within 10 percent. This percent indicates an acceptable range of analytical error. The balance is based on charge (meq) rather than weight (mg/L). *Example:*
Na^+ 3.7 + Ca^{2+} 2.2 + Mg^{2+} 0.5 + K^+ 0.0 + NH_4^+ 0.0 = 6.4;
SO_4^{2-} 0.7 + NO_3^- 0.1 + Cl^- 0.6 + HCO_3^- 5.0 = 6.4.

Atomic weight is the weight in grams of 6.022×10^{23} of a particular element. This weight can be found for each element on a periodic table or in the back of most chemistry books.

Molecular weight is the mass of one mole of a substance. This can be calculated by summing the atomic weights of each atom in a molecule. *Example: the molecular weight of NaCl is the atomic weight of Na^+ plus Cl^-. Therefore, 22.9898 + 35.4530 = 58.4428 g/mol.*

Electrical conductivity (EC) describes how well a charge of electricity crosses 1 cm of water. EC is proportional to dissolved salts. Because this measurement is quicker and easier than a direct laboratory analysis, it is often used to estimate total dissolved solids or total soluble salts.

Total dissolved solids (TDS) is defined by its laboratory method where a known volume of water is filtered and evaporated, leaving the dissolved solids. These solids are weighed, divided by volume and reported in mg/L. Most laboratories simply estimate TDS from EC. The 0.45 micron filter is the laboratory standard for removing undissolved particles and retaining dissolved solids in water.

Total soluble salts (TSS) is the sum of all anions plus cations as mg/L. Alternatively, and more commonly, TSS can be estimated from EC.

Total suspended solids (TSS) is the weight of solids filtered from a liter of water. Having a second TSS term is confusing; however, this version is primarily used by water treatment plants.

Sodium hazard is the risk that sodium breaks down soil structure by replacing calcium and magnesium in the soil. When soil structure breaks down, infiltration rates suffer.

Sodium adsorption ratio (SAR) is an index of the sodium hazard in irrigation water, and it is calculated using a ratio of sodium to (calcium plus magnesium).
SAR has two weaknesses. First, SAR underestimates the sodium hazard when the total salts are very low; with this condition, soil salinity samples should be routinely monitored for accumulation of sodium in the soil. Second, SAR underestimates the sodium hazard when water with moderate or high bicarbonate concentrations precipitate calcium from the solution.

Residual sodium carbonate (RSC) is an index of the carbonate and bicarbonate hazard in irrigation water. When irrigation water contains high concentrations of carbonates and bicarbonates, they can precipitate the calcium and magnesium out of solution and change the sodium hazard. However, RSC is an obsolete index because it fails to use chemical equilibrium reactions; adj SAR is more appropriate.

Adjusted sodium adsorption ratio (adj SAR) is a sodium hazard index adjusted for the solubility of calcium carbonate. When calcium and carbonate concentrations are high

enough to precipitate calcium carbonate out of a soil-water solution, SAR underestimates the true ratio; the adj SAR raises the ratio to a more realistic value. However, few laboratories include adj SAR on their reports because the adjustment is complex.

Adjusted sodium adsorption ratio (adj RNa) is another adj SAR. This term could represent any number of adjustment techniques; therefore, adj SAR is still used as the standard term.

Exchangeable sodium percent (ESP) is a soil term that measures the sodium hazard in soil. This is a time-consuming laboratory analysis, so ESP is commonly calculated from SAR.

Water hardness is a rating system that defines how much calcium and magnesium are in water. This system is important because hard water forms calcium carbonate deposits on sprinkler heads.

Total phosphorus (P) is all forms of P reported from a digested, unfiltered sample.

Total dissolved phosphorus is all soluble forms of P, including organic P, in a filtered sample.

Orthophosphate is soluble phosphate (PO_4^{3-}) in a filtered sample. Orthophosphate analysis is an easy and reliable method; however, it fails to measure other forms of P, such as organic P.

Nitrate (NO_3^-) and **nitrite (NO_2^-)** are two forms of nitrogen in water; however, nitrate is a common anion form of inorganic nitrogen, while nitrite is an uncommon anion form. With normal conditions, nitrite is quickly converted to nitrate.

Nitrate as nitrogen (NO_3-N) is a common way of reporting nitrate where only the weight of the N is considered. This reporting is helpful because various forms of nitrogen can easily be added together for a nitrogen budget.

Ammonium (NH_4^+) and **ammonia (NH_3)** are two forms of the same thing, differentiated by pH. In an acid solution, the form is ammonium; in a basic solution, the form is ammonia. For most purposes the difference is irrelevant; however, the ammonium form is more stable in water.

Ammonium as nitrogen (NH_4-N) is similar to NO_3-N; both consider only the weight of the N.

Sulfate (SO_4^{2-}) and **sulfite (SO_3^{2-})** are two forms of sulfur in water. However, sulfur usually takes the form of sulfate in water.

Sulfate as sulfur (SO_4-S) is similar to NO_3-N; only the weight of S is considered.

Units

mg/L (milligrams per liter) is used when quantifying the weight (in milligrams) of a particular ion per liter of water. Keep in mind that a milligram is 1/1,000 of a gram. *Example: 1,000 mg/L Na^+ = 1 g/L Na^+.*

ppm (parts per million) is similar to mg/L, but instead of a weight to volume ratio, ppm is a weight-to-weight ratio. It is the milligrams of a substance in 1,000,000 mg of water (1,000,000 mg of water equals 1.000 liter of water). Because of this weight-to-weight relationship, it is a dimensionless term. The ppm unit approximates mg/L; still, the two terms are often used interchangeably.

% (percent) often replaces ppm when ppm concentrations are very high. The ppm is converted to percent by dividing ppm by 10,000. *Example: 20,000 ppm ÷ 10,000 = 2.00 %.*

mg/kg (milligrams per kilogram) is the same as ppm; however, these are units of a solid, such as soil, and are seldom used in water measurements.

meq (milliequivalents) is the weight of an ion in water converted to its charge equivalence. This is accomplished by multiplying the mg/L of the ion by the absolute value of its charge and dividing by its atomic weight. *Example: Ca^{2+} is a divalent ion with an atomic weight of 40.078; therefore, 100 mg/L Ca^{2+} × |2+| ÷ 40.078 = 4.99 meq/L.*

mmol/L (millimoles per liter) is the molecular weight of an ion or a molecule in a liter of water. To convert mg/L Na^+ to mmol/L Na^+, take the mg/L and divide by the atomic weight of Na^+. *Example: 100 mg/L Na^+ ÷ 22.989 = 4.35 mmol/L Na^+.*

µS/cm (microsiemens per centimeter) is the international unit for electrical conductivity. This unit is the same as the traditional unit, µmhos/cm; either unit can be expressed as milli- as well. Additionally, scientific literature often uses decisiemens per meter (dS/m) in place of mS/cm. *Example: 1 µS/cm = 1 µmhos/cm = 0.001 mmhos/cm = 0.001 mS/cm = 0.001 dS/m.*

Equations

Electrical conductivity (EC)

EC µS/cm × 0.64 = TDS mg/L or TSS mg/L (other factors similar to 0.64 are also used, especially with higher levels of EC).

Residual sodium carbonate (RSC)

RSC meq = (HCO_3^- meq + CO_3^{2-} meq) − (Ca^{2+} meq + Mg^{2+} meq)

Sodium adsorption ratio (SAR)

$$SAR = Na^+ \text{ meq} \div \sqrt{(Ca^{2+} \text{ meq} + Mg^{2+} \text{ meq}) \div 2}$$

Adjusted sodium adsorption ratio (adj SAR)

The details of this "simplified" calculation can be found in Lesch and Suarez (2009), *A Short Note on Calculating the Adjusted SAR Index*.

1. Convert Na^+, Ca^{2+}, Mg^{2+}, and HCO_3^- to meq/L
2. Calculate ionic strength (I_S)
   I_S = ((1.3477 × (Na^+ + Ca^{2+} + Mg^{2+})) + 0.5355) ÷ 1,000
3. Calculate log(X)
   Log(X) = 0.3333 × (4.6629 + 0.61031 log(I_S) + 0.0844 × (log(I_S))^2 + 2 log(Ca^{2+} ÷ (2 HCO_3^-)))
4. Calculate the calcium equilibrium concentration
   Ca^{2+}_{eq} = 2 × $10^{\log(X)}$ × $(P_{CO_2})^{1/3}$
   Replace the Ca^{2+} term in the SAR equation with Ca^{2+}_{eq}

Exchangeable sodium percent (ESP)

$$ESP \text{ (from SAR)} = -\frac{100 \, (-0.0126 + 0.01475 \times SAR)}{1 + (-0.0126 + 0.01475 \times SAR)}$$

Water hardness (as $CaCO_3$)

$CaCO_3$ mg/L = (Ca^{2+} meq × 50) + (Mg^{2+} meq × 50)

The Instrumentation of Water Quality

Laboratory instruments measure elements in water, using seven basic techniques: spectrophotometry, atomic spectrometry, chromatography, titration, potentiometry, gravimetry and field.

Spectrophotometry is probably the most important and commonly used technique in water quality analysis. Spectrophotometers measure individual nutrients by emitting light through a sample. First, the sample is colored using a chemical reaction; the higher the concentration, the darker it gets. The spectrophotometer then passes light through the colored sample and measures the remaining light. The amount of light that is absorbed corresponds to nutrient concentration.

Modern spectrophotometers are normally automated for efficiency and consistency. There are four commonly used automated systems: continuous-flow analyzers, flow-injection analyzers, discrete analyzers and plate readers.

Continuous-flow analyzers (CFA) insert bubbles between each sample to analyze them consecutively. These analyzers mimic the manual process described above. The continuous flow analyzer was one of the first auto-analyzers for the spectrophotometric technique. This system has largely been replaced by other automated systems.

Flow-injection analyzers (FIA) use a valve with a sample loop to produce a consistent sample size, and they automate the rest of the spectrophotometric process. The FIA can analyze a large a number of samples quickly and accurately. It can measure more than one element at a time.

Discrete analyzers fully mimic manual spectrophotometry in an automated process. These systems can consecutively measure multiple elements in separate micro cups.

Plate readers were designed for microbiology work to read many samples simultaneously. However, they have been adapted to do spectrophotometric analysis. They can analyze samples quickly and economically and are relatively inexpensive compared to other automated systems.

Atomic spectrometry can be absorbance (similar to spectrophotometry) or emission. Atomic emission spectrometry uses intense heat to energize electrons in a water sample to higher energy states. As the electrons cool, they return to their original energy state and give off light. The wavelength and intensity of that light is used to identify and quantify elemental concentrations in the water sample. This technique is often used to measure base cations. These instruments come in two varieties: flame- or plasma-based.

Atomic emission spectrometers (AES) aspirate the sample into a flame to energize the electrons. This instrument is fast and inexpensive to operate, but it normally measures only one element at a time.

Inductively coupled plasma (ICP-AES) is an advanced form of AES. The ICP aspirates a sample into plasma (very hot) instead of a flame (hot). This is cost-effective for analyzing multiple elements simultaneously.

Chromatography is a technique that originated from pigment separation in chlorophyll. When a drop of chlorophyll extract is placed on the bottom edge of a piece of absorbent filter paper, which is then placed in a solvent, the different colors in the chlorophyll will separate into bands as the solvent travels up the paper. Instead of colors, an ion chromatograph separates ions into bands, measures those bands sequentially and quantifies their concentrations.

Chromatography is a powerful technique for measuring anions in water because it measures multiple elements in a single analysis. However, each sample analysis takes a minimum of seven minutes, which is too long for a production laboratory.

Titration uses an acid or base to measure specific ions in the water. The ion concentration is calculated by the amount of acid or base (called a titrant) added to reach a specified pH.

Titrations are commonly used in water analysis to measure carbonates and bicarbonates. These are determined by lowering the pH of a water sample to 8.2 for carbonates and 4.4 for bicarbonates. The carbonate and bicarbonate concentrations are used for calculating RSC and correcting SAR.

Potentiometry instruments use ion-specific electrodes that produce a voltage when placed in a water sample; the greater the specific ion's concentration, the stronger the voltage.

The pH electrode is one the most important and reliable examples of an ion-specific electrode. This electrode measures the H^+ ion's concentration, and the instrument converts the voltage into a negative log scale (a 10-fold increase in H^+ equals a single unit decrease in pH).

The electrical conductivity (EC) electrode is also reliable, but it's a special case in potentiometry. This electrode is not ion-specific and only estimates total ions and TDS. Other ion-specific electrodes (e.g. for nitrate, ammonium and chloride) are inexpensive and available, but troublesome.

Gravimetry analysis uses scales to weigh a sample before and after evaporation; this gives the total weight of solids in the sample. TDS is a product of this technique.

Field techniques are modified and simplified laboratory techniques. Field instruments and test kits include portable meters, electrodes and chemical packets for measuring a wide variety of elements. Most of these elements are best left for laboratory personnel and instrumentation. However, electrical conductivity meters are easily and reliably maintained and calibrated in the field.

For Further Reading

The following reference list covers the interpretation of water quality reports:

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