Technical Note 4.
Understanding Soil pH: Theory, Measurement, Application

4.0 Background

pH is one of the most commonly measured soil chemical properties. Technically, pH is a measure of hydrogen ion activity in a solution. pH, also called soil reaction, describes the acidity or alkalinity of soil. Unfortunately, soil pH is an elusive, often misunderstood concept. This is due, in part, to the fact that pH measures something we cannot see. No human has ever seen a "hydrogen ion", even with the most powerful microscope. We only understand the *effects* of hydrogen ions in solution. Because no one can see hydrogen ions, we must return to the fundamentals, or "first principles", of atomic behavior to develop a systematic, logical way of reasoning. Understanding the basics strengthens our ability to observe and measure accurately, which in turn allows us to diagnose problems more effectively.

4.1 Atoms and Electrons: The Basics

Our modern understanding of atomic structure is based on nuclear theory. It's called a theory because, as previously noted, no human has seen an atom to verify the details of its structure. The atomic theory holds that an atom is composed of a dense, central core called a nucleus, containing positively charged ***protons***, neutral particles called ***neutrons***, surrounded by less dense, negatively charged particles called ***electrons***. The electrons are scattered around the nucleus in stable orbits, like the planets in our solar system. An attractive ***electromagnetic*** force holds the positively charged nucleus and the negatively charged electrons together. Now, we must understand that this force does not always bind all the electrons to the nucleus. Those electrons in the outer orbits of some elements are loosely held and are called "free electrons" (**Figure 4.1**). That is, they can move freely from one atom to another. They may wander at random or move to a neighboring atom or molecule.

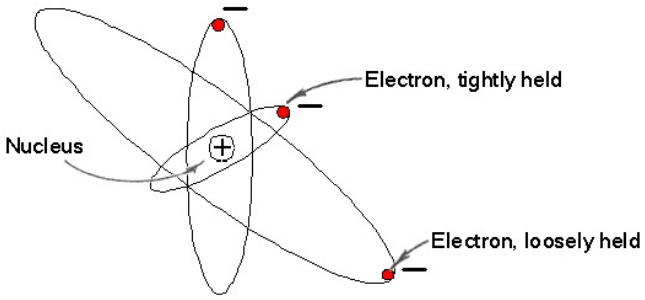


Figure 4.1 Two-dimensional Bohr model of an atom. Named after Danish physicist Niels Bohr (1885-1962) who contributed to our understanding of the fundamentals of atomic structure and quantum mechanics in the early 20th century.

The nucleus usually has a positive charge equal to the negative charge of all the electrons in its orbit. An atom in this state is said to be balanced, or *neutral,* with respect to its charge. However, when electrons start to move away from the nucleus, the loss of electrons causes the atom to acquire a net positive charge. On the other hand, if a surplus of electrons moves into the orbit of an atom, the opposite thing happens. The atom acquires a net negative charge. When an atom gains or loses electrons, it becomes an ***ion***, as it now has a net positive or negative charge. Keep this idea tucked away for the future. As it happens, the treatment of soil fertility leans heavily on ions and ionic states of both atoms and molecules.

Hydrogen (chemical symbol **H**) is quite a simple atom consisting only of one proton and one electron. The lone electron in its orbit is loosely bound and free to wander. Hydrogen ions are produced when a hydrogen atom loses an electron, leaving it in an ionic *state* with a net positive charge. We denote this net positive charge by writing H^+, meaning a *hydrogen ion*. These are the ions we measure in pH (conversely, a negative sign indicates an atom with a surplus of electrons).

Another chemical concept we need to comprehend is that of a ***solution***. During this project, we may develop and analyze solutions. We need to understand what this means, so communications about the soil are understood by all. A solution exists in the soil by virtue of its water content. When we measure soil pH, we measure the chemical property of water and the ions dissolved in it. The solid phase of the soil, consisting of sand, silt, clay, and organic matter, is not directly involved. When we dissolve sodium chloride (NaCl, or table salt) in water, the sodium and chloride dissociate as Na^+ (a positively charged ***cation***) and Cl^- (a negatively charged ***anion***)—the mixing of salt and water results in a solution. Thus, we can speak of the *soil solution* as a mixture of water plus ions (and a few other molecules). Now that we comprehend how ions and solutions are formed, we can move on to pH and its relationship to soil fertility.

The pH of a solution is defined as:

$$-\log(H^+)$$

where –log is the negative logarithm to the base ten, and (H^+) is the *active* concentration of hydrogen ions in the solution. Ion *activity* refers to chemical potential, or the "freedom" of ions to interact with other ions in solution. Active hydrogen ions are "free" in the sense that they may interact with other ions or molecules in a solution. In aqueous (water-based) solutions, there is strong evidence that hydrogen ions do not exist as H^+ but rather exist as hydronium ions, H_3O^+. Hence, there is some ambiguity about how to write and speak of the "hydrogen ion". When referring to the acidity of a solution, agronomists use "hydrogen ion activity," which is understood to mean the free H^+ ions that can produce acidity.

Concentration is the amount of a substance (ions or molecules) per unit volume of solution expressed as ***moles per liter*** (mol L^{-1})[1]. In dilute soil solutions, the hydrogen ion activity (H^+) is approximately equal to its concentration [H^+] in mol L^{-1}. Therefore, we can write:

$$pH \approx -\log[H^+] \text{ or } \log\frac{1}{[H^+]}$$

Note that in chemistry notation, parentheses ( ) are used to represent activity and brackets [ ] to represent concentration.

Water molecules have a natural tendency to split apart, or ***dissociate***, releasing hydrogen and hydroxyl ions:

$$\underset{\text{water}}{HOH\ (H_20)} \rightleftharpoons \underset{\text{hydrogen}}{H^+} + \underset{\text{hydroxyl}}{OH^-}$$

The ***equilibrium constant*** for water K_w is [H^+] x [OH^-] and has a product of 10^{-14} moles per liter at 25°C. In pure water, [H+] = [OH-] = 10^{-7} mol L^{-1}, and the pH is 7, which is neutral. An input of acid (for example, HNO_3 (nitric acid) raises the H^+ concentration, causes some association of H^+ and OH^- to form water, and leaves the [OH^-] less than 10^{-7}, [H^+] greater than 10^{-7}, and pH less than 7. The interesting thing is that regardless of the quantity of acid or base added to pure water, the product of [OH^-] x [H^+] will always be 1 x 10^{-14} ! Because of this property, we can always calculate the [OH^-] if we know [H^+], and vice versa.

Using the "p" scale (negative logarithm) is a convenient way to express hydrogen ion concentration, since hydrogen ion concentrations are very small. The use of negative logarithms allows us to convert a negative power of ten into a small positive number. Thus, the solution pH is defined on a logarithmic scale ranging from 0 to 14 (small positive values). This means that a solution at pH 5.0 has a hydrogen ion concentration *ten times* greater than a solution at pH 6.0. Likewise, a solution with pH 4.0 has a hydrogen ion concentration *one hundred times* greater than a solution at pH 6.0. The pH range of soil solutions varies from about 3.5 to 10 ($10^{-3.5}$ – 10^{-10} mol H^+ per liter). **Table 1** (link) shows the relationship between pH, the concentration of H^+ and OH^-, and scientific notation.

An *acid* is a substance that is a source of H^+ in solution, whereas a *base* is a substance that may combine with H^+. Suppose sodium hydroxide (NaOH, a strong base) is added to water such that its final concentration is 0.01 mol L^{-1}. In that case, the concentration of OH^- is also 0.01 mol L^{-1}, and the equilibrium concentration of H^+ is diminished according to the equation:

$$[H^+] = K_w/[OH^-] = 10^{-14}/10^{-2} = 10^{-12}$$

The pH of this solution is:

$$pH = -\log[10^{-12}] = 12.$$

This high pH indicates that the 0.01 M NaOH solution is strongly alkaline with a low concentration of H^+ ions.

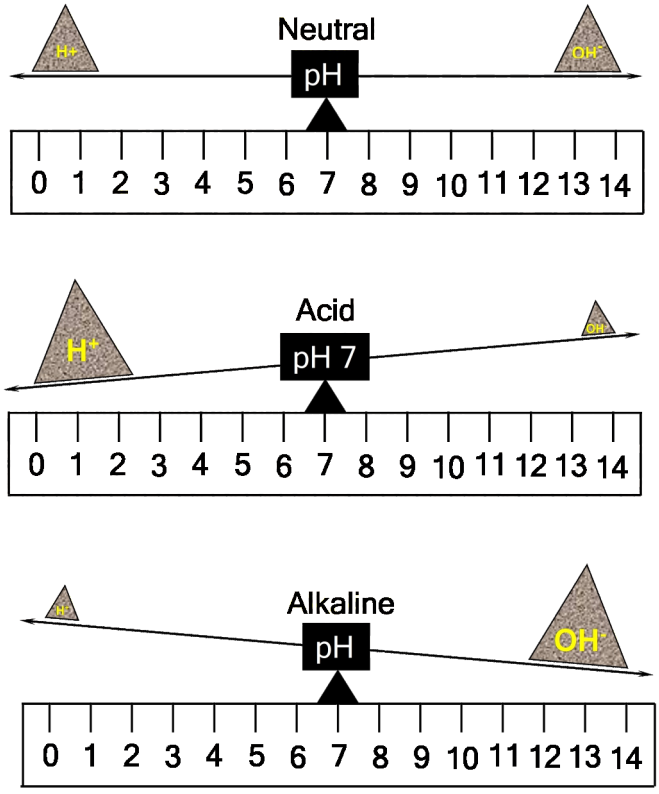
[1] A negative exponent following a compound (derived) unit of measure is mathematical notation for the reciprocal: $a^{-n} = 1/a^n$ "take the reciprocal and make the exponent positive". Thus mol/L^{-1} is read "number of moles per liter" i.e., concentration per unit volume. We use this notation hereon to describe the concentration of atoms/molecules.

Water will absorb CO_2 from the atmosphere, which reacts to form carbonic acid, H_2CO_3. This is a weak acid and partially dissociates to release H^+, HCO_3^- and CO_3^{-2}:

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

Pure water in equilibrium with CO_2 at the atmospheric concentration (0.03% *v/v*) has a pH of 5.6. A soil solution has a pH below or above 5.6 if the soil is acting as an acid or a base. This is an essential concept to grasp.

Soil is said to be *acidic* if it contains an excess of H^+ ions in solution or can generate them. A *basic,* or *alkaline,* soil has an excess of OH^- ions in solution or can generate them. A *neutral* soil has a balance of H^+ and OH^- in solution and would have a pH near 7. When the soil is too acidic or too alkaline, some people say the pH is "out of balance". Balancing soil pH does not mean adjusting it to 7. Soils are not balanced with respect to pH; they are adjusted to "target" pH values determined by soil type and the specific crop being grown. Nevertheless, using the balance analogy, we can figuratively represent pH as follows:



Soil *buffering capacity* is the ability of soil to resist a change in pH when an acid or base is added. Adding acid or base to a poorly buffered soil causes a larger shift in pH than adding the same amount to a highly buffered soil. Sandy soils are poorly buffered. The pH will drop after fertilization but will soon exhibit the pH of the water surrounding the sand particles. Clayey soils and/or soils with high organic matter are strongly buffered and more resistant to pH-altering influences.

4.2 Factors Influencing Soil pH

Soil acidity or basicity is modulated by several factors, principally:

- Nature of the parent materials from which the soil was formed. Soils developed in the residuum of acid rock (e.g. granites) are generally sandy textured with fewer basic cations. These conditions favor acidification. In contrast, soil derived from basic rock (e.g. basalt, limestone) favor a basic reaction[2].
- Precipitation level. Water passing through the soil leaches basic cations such as calcium (Ca) and magnesium (Mg) into drainage water. They are replaced by acidic elements such as hydrogen (H), manganese (Mn), and aluminum (Al). Soil formed in humid areas is more acidic than that formed under arid conditions. In general, soils of the eastern United States where rainfall exceeds evaporation are acidic. Many soils of the drier western United States are basic.
- Soils developed under forest vegetation tend to be more acidic than those developed under grassland. Evergreens (conifers) produce greater acidity than deciduous forests. Nutrient uptake by plants also contributes to soil acidification because cations absorbed by roots are balanced by an equivalent release of H^+ by the roots to maintain electrical neutrality.
- Soil becomes more acidic as crops remove basic nutrients like K, Ca, and Mg. Legumes generally contain higher amounts of Ca and Mg than non-legumes. Calcium and magnesium content also vary in other parts of the plant.
- Acidity generally increases with soil depth and loss of topsoil by erosion, and may increase acidity in the plow layer. As the depth of topsoil decreases, more subsoil is mixed within the plow layer. This increases acidity.
- Fertilization, especially with ammonium-N fertilizers, increases acidity. On calcareous soils, the acidifying effects from fertilization can be beneficial.
- Nitrogen fixation by symbiotic bacteria that colonize the roots of legume plants contributes to soil acidification.
- Decay of organic increases soil acidity. One of the first products formed during organic matter decomposition is ammonia. When ammonia is converted to nitrate through nitrification, H^+ is released. This process is illustrated below (the effect of adding fertilizer ammonia is similar):

$$2NH_3 + 3H_2O \xrightarrow[\text{bacteria}]{} 2NO_3^- + 6H^+$$

Decaying organic matter also releases CO_2 which reacts with water to form carbonic acid, further contributing to acidification:

$$\underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2} \rightleftharpoons \underset{\text{carbonic acid}}{H_2CO_3}$$

[2]The terms "acid" and "basic" rock refer to the silica content of the rock material, not chemical acid-base reaction. In geology these terms have been replaced by "Felsic" and "Mafic" respectively although the old terminology is still used.

4.3 Measuring Acidity

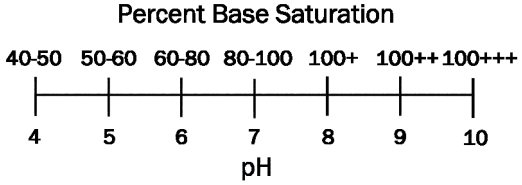
Two attributes of soil acidity can be measured. First is *active acidity*, characterized by the measurement of H^+ ions in solution expressed as pH. Methods for measuring active acidity vary, but commonly involve mixing soil + water in a predetermined ratio and reading the results on the display of a pH meter. Second is *exchangeable acidity*, characterized by the presence of H^+ and trivalent aluminum (Al^{+3}) associated with soil minerals. Methods for measuring exchangeable acidity also vary and may involve mixing soil with a solution of dilute $CaCl_2$ (calcium chloride) or KCl (potassium chloride) or determining exchangeable acidity analytically by measuring the quantity of alkali required to **titrate** the soil to a predetermined endpoint.

When soil is mixed with a solution of $CaCl_2$ or KCl, the calcium and potassium exchange places with hydrogen and aluminum on ***soil colloids***. The hydrogen ions are released into solution; the aluminum ions hydrolyze in water, releasing more hydrogen ions. When this exchange is complete, the solution's pH will be lower than when measured with a mixture of water + soil alone. The quantity of exchangeable acidity is used to calculate the lime requirement of a soil, e.g., the quantity of lime needed to neutralize exchangeable acidity and adjust soil pH to its "target" value (see Technical Note 3).

Measurement of hydrogen ion activity in a mixture of soil and water may express the soil's need for lime, but cannot predict the number of pounds per acre to apply. Moreover, hydrogen ions alone do not manifest a direct toxic effect on plant growth unless soil pH drops below ~3. This rarely happens unless strong acids (usually man-made) are introduced to the soil. At this point, you may be wondering, 'Why measure soil pH at all?' But there's more to the story...

Whether soil is acidic, basic, or neutral has much to do with the *solubility* of plant nutrients, the proportion of nutrients bound to soil colloids in *exchangeable* form, the net charge (positive or negative) of certain soil colloids, and the activity of various microorganisms. As soil becomes more acidic the following changes take place:

- The amounts of exchangeable K^+, Ca^{2+} and Mg^{2+} decrease. These, together with Na^+ and NH_4^+, are known as base, or nonacid, cations (recall a cation is an ion with a net positive charge). The total amount of base cations associated with soil solids (specifically, the *colloidal* fraction) is often expressed as a percentage of the soil's *cation exchange capacity*, termed *base saturation*. The percentage base saturation (% BS) indicates *how* much of the soil's nutrient-holding capacity is being utilized. There is an inverse relationship between soil pH and percentage base saturation: as the concentration of exchangeable H^+ and Al^{+3} increases, the percent base saturation decreases, and vice versa.



- The amount of exchangeable trivalent aluminum (Al^{3+}) increases and is often expressed as the *percentage aluminum saturation*. Soluble Al^{3+} has a direct toxic effect on root growth and, in turn, nutrient uptake.
- The negative charge on humus decreases, and the positive charge on iron-enriched minerals (called ***sesquioxides***) increases.
- The solubility of plant nutrients is altered. For example, at low pH (<6.0) the solubility of phosphorus is decreased. The solubility of elements such as aluminum and manganese increases whereas, the solubility of zinc and copper decreases. The opposite is true at high pH (>6.0).
- The activity of many soil organisms is decreased, resulting in reduced mineralization of organic matter, lower availability of nitrogen, phosphorus, and sulfur.

Here we come upon a dilemma. While the effects of pH on soil fertility are understood, this does not tell us which nutrients may be lacking, in adequate supply but unavailable, or in excess. The most we can say at this point is that pH is an indirect indicator of soil fertility. We need a quantitative analysis of soil acidity and nutrients to determine what additions or subtractions might be required to bring the soil into "balance". Only a soil test can furnish this piece of the puzzle.

There's one more caveat. We measure soil pH with a pH meter. The precise numerical values commonly obtained from pH meters convey the false idea that soils have characteristic pH values. In reality, a range of pH values may be observed for a given soil sample. Varying the soil/solution ratio, equilibration times, time of sampling, and addition of neutral salts such as $CaCl_2$ or KCl, all tend to yield different results. Moreover, the presence of fertilizer salts in a soil sample will depress pH readings. Therefore, it is essential to know where fertilizer bands are located to avoid pH readings that are biased. Despite this complexity, the interpretation of soil pH values can be justified by uniform sampling, measurement, and correlation with other soil properties.

4.4 Measuring pH

pH can be measured using an ion-sensitive glass ***electrode***, a reference electrode, and a pH meter, which is a millivoltmeter (i.e., it measures very, very small voltages). **Figure 4.4.1** shows a schematic of this arrangement. When there is a difference of pH between the solution inside and outside the bulb of the glass electrode, an electric ***potential*** develops across the glass membrane. The potential arises because of ***ion exchange*** between ions in the glass and H^+ ions in the solution. This can only be measured relative to another reference potential. An electrode containing a mixture of mercury (Hg), mercurous chloride (Hg_2Cl_2, or 'calomel') and potassium chloride (KCl) can be utilized as a reference.

The potential difference between the electrodes is measured in millivolts and varies linearly with the solution's pH. The meter is then calibrated to give a pH reading. The two-electrode half-cells are often manufactured as a single *combination* electrode (**Figure 4.4.2**).

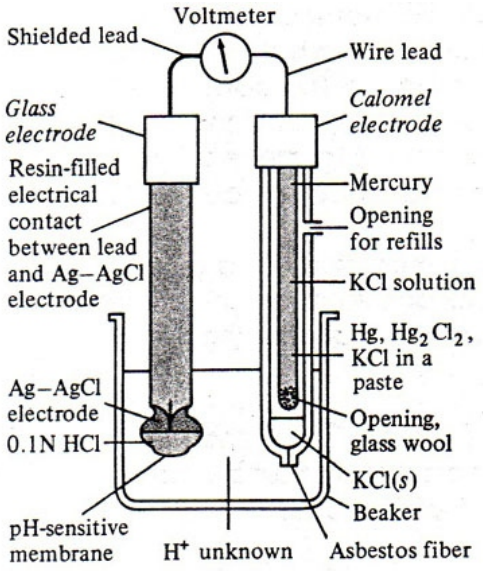


Figure 4.4.1 pH meter schematic.

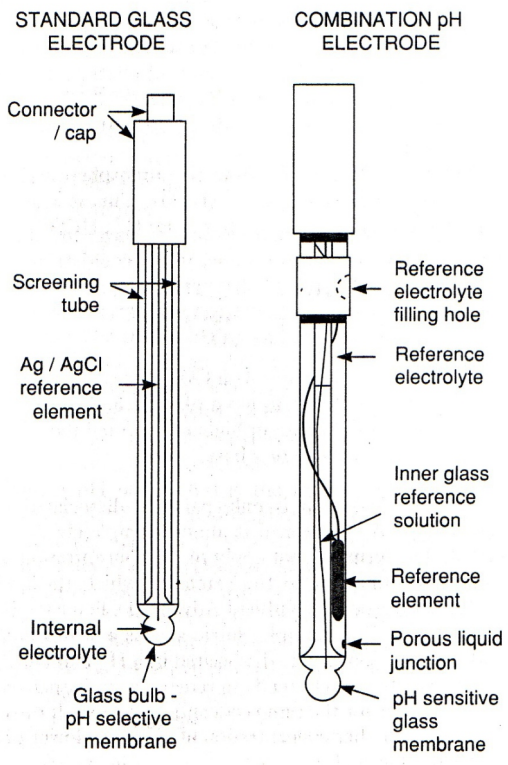


Figure 4.4.2 Standard and combination pH electrode.

The ion-sensitive half-cell includes a ***buffer solution*** with a fixed pH and ionic strength. A wire coated with silver chloride (AgCl) is immersed in this internal solution and establishes electrical contact between the solution and the meter. The voltage associated with this wire, the pH of the internal solution, and the inside wall of the H^+-sensitive glass tip remain constant. Therefore, changes in voltage from this electrode arise from the potential difference between the solution and the exterior of the glass tip. The wire dipping into the reference half-cell contacts the pH meter, and current flows from the reference half-cell back to the test solution. Diffusion of KCl through the orifice of the reference half-cell makes contact with the test solution to complete the circuit. The potential of the reference electrode is independent of pH and is assumed to be constant.

Since potentials are, in general, independent of the physical size of the electrodes, the electrodes can be miniaturized, allowing the measurement of small solution volumes. Moreover, small pH meters (so-called 'pocket' meters) are possible and have been introduced for field use.

Ambient temperature also affects the pH of a solution. At 100°C, the pH of pure water is 6.0, and at 0°C, it is 7.5. The factory default setting on most pH meters is 25°C. If the test solution is not 25°C, a temperature-compensated probe (ATC) is required for accurate results. Some pH meters come with a separate probe, while others accept electrodes with a built-in ATC probe. Both Orion 290A portable and pHep pocket pH testers have built-in temperature compensation (**Figure 4.4.3**). Check the manufacturer's spec sheet on temperature compensation when in doubt.

pH meters must be calibrated before use. The ability to calibrate a pH meter allows the meter to match its millivolt reading to the known pH of a buffer solution and display that millivolt reading as a pH value we can interpret (we can't very well interpret millivolt readings!). For best accuracy, at least two buffer solutions bracketing the expected pH of the unknown test solution are required. A mathematical function is derived relating the change in millivolts per unit change in pH. The ***slope*** of the function indicates how closely the relationship between the expected voltage at the buffer pH and the actual voltage matches. On pocket meters, the slope output may not be visually apparent. Laboratory-grade pH meters may have a manual slope adjustment knob or an automatic reading displayed after calibration. Most accurate readings of pH are obtained when the electrode slope is between 92% and 102%. Readings from an electrode operating outside these limits may be erroneous, although the electrode will continue working.

Troubleshooting pH meters is beyond the scope of this technical note. However, most problems with pH meters are electrode-related. Failure of pH readings to stabilize can usually be traced to a malfunctioning electrode. The electrode should be inspected, the level of the reference solution checked, and the electrode cleaned thoroughly with distilled water. If the readings still don't stabilize, replace the electrode.

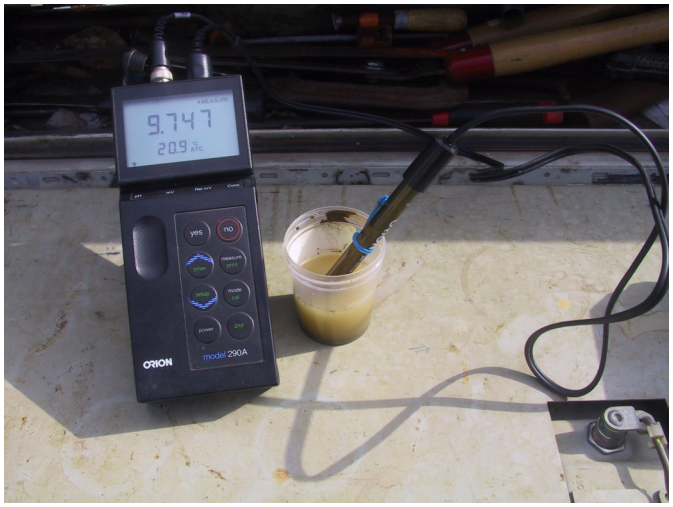


Figure 4.4.3 Portable meters like the one shown here are invaluable for on-the-spot soil chemical properties determination, including pH.

4.5 Core Intelligence

Anion: A negatively charged ion, formed by the addition of electrons to atoms or molecules and denoted by a negative sign (-). The valence is indicated by a whole number either before or after the negative sign. For example, NO_3^- (nitrate ion) has a valence of 1; SO_4^{-2} (sulfate ion) has a valence of 2. Anions with a valance of 1 are termed *monovalent,* a valance of 2 *divalent*, a valance of 3 *trivalent*, and so on.

Buffer Solution: A solution that is formulated to resist change in pH when small quantities of acid or base are added to it.

Cation: A positively charged ion, formed by loss of electrons from atoms or molecules and denoted by a positive (+) sign. The valence of a cation is indicated by a whole number either before or after the negative sign. For example, Ca^{+2} (calcium ion) has a valence of 2. Cations with a valance of 1 are termed *monovalent,* a valance of 2 *divalent*, a valance of 3 *trivalent*, and so on.

Concentration: The amount of a substance per unit volume in a solution.

Dissociate: The breakdown of one molecule into two molecules, atoms, radicals, or ions. The reaction is often reversible. A reversible chemical reaction is denoted by arrows pointing in two directions ( ).

Electron: An atomic particle of negative charge and negligible mass. Electrons are present in all atoms in shells, or orbits, around the nucleus.

Electrode: A solid electric conductor through which an electric current enters or leaves a medium such as an electrolyte, a non-metallic solid, a molten metal, a gas, or a vacuum.

Electromagnetic Force
The universal force acting between electrically charged particles. It's responsible for light, electricity, magnetism, and all chemical reactions. The attraction between protons and electrons in atoms is *electrostatic*, a special case of the electromagnetic force acting on stationary electric charges. It holds molecules together and creates virtually all the properties of everyday materials.

Equilibrium constant: The equilibrium concentration of reactants and products in a reversible reaction. Given by the generalized equation:

$$K = \frac{[R]^r[S]^s}{[A]^a[B]^b}$$

where [R] [S] and [A] [B] are the products of the concentration in moles per liter of the products and reactants, respectively, raised to the power equal to their stoichiometric coefficients (e.g., $2H_2O$ has a constant coefficient 2) Equilibrium constants have different forms depending on the nature of the products and reactants; they may change with changes in temperature and pressure.

Humus: The fraction of the soil organic matter remaining after the central portion of added residues has decomposed. Usually amorphous and dark colored.

Hydrolyze: A reaction between a compound and water in which the water molecule is split.

Ion: Atoms or groups of atoms that are electrically charged because of the loss of electrons (cations) or the gain of electrons (anions).

Ion Exchange: A process that takes place in certain soil solids such as clays and organic matter, which contain ions capable of exchanging with ions in the surrounding solution.

Linear(ly): A relationship between two variables *xy* that can be modeled by the straight-line equation $y=ax+b$ where *a* is the *slope* (constant of proportionality) and *b* is the point where the line crosses the *y* axis (*y*-intercept). When $b=0$ the line passes through the origin (0,0) the relationship is proportional, i.e. slope $a=1$. *All proportional relationships are linear* but not all linear relationships are proportional.

Mineralization: The conversion of an element from an organic form to an inorganic form because of microbial decomposition.

Moles per liter: unit of concentration of a substance equal to the gram molecular weight of that substance dissolved in one liter of water. A centimole (cmol) is $1/100^{th}$ of a mole and, when speaking of atoms in ionic state, is numerically equivalent to the older unit milliequivalent per liter (meq).

Neutron: A neutral particle of mass 1.674929×10^{-27} kg found in the nucleus of an atom.

Potential: The energy of a particle or system of particles derived from position, rather than motion, with respect to a specified datum in a field of force.

Proton: A positively charged elementary particle of mass 1.67262×10^{-27} kg found in the nucleus of an atom. The mass of protons and neutrons is nearly equal.

Sesquioxide: A term for minerals containing 1.5 atoms of oxygen per atom of metal. Aluminum and iron are common metal constituents of sequioxides.

Soil colloid: Generally, a very finely divided particle forming a stable dispersed phase when dissolved in another continuous medium. Clay and organic matter are the colloidal fraction of the solid phase of soil. When clay is dispersed in water, it forms a stable suspension that does not settle out quickly.

Solute: A material that is dissolved in a solvent to form a solution. Table salt (NaCl) is the solute when it is dissolved in water (the solvent) to form a salt solution.

Solution: A liquid system of two or more substances that are intimately dispersed within each other at the molecular level.

Slope: In mathematics, slope is a measure of the steepness or incline of a line, representing how much the line rises or falls as you move horizontally.

Titrate: To find the concentration of an unknown substance by adding a known volume of another substance of known concentration until the equivalence point or endpoint is reached. Indicator dyes that change colors are used to determine the endpoint.

Further Reading

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