**Research Article**

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# Broadening Perspective of Soil Acidity in Plant-Soil Systems

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**Core Ideas**

1. Hydrogen ions ($H^+$) are protons, composite particles comprised of quarks stabilized by gluons.

2. Hydrogen ions are Lewis-acids that react with Lewis-bases forming Lewis acid-base adducts.

3.  Lewis acid-base adducts such as hydronium ($H_3O^+$) are sources of acidity in plant-soil systems.

*Abstract*

*Acidity is an environmental pressure shaping the fitness of soil for plants including turfgrasses. Details on pH and its measurement appear in the plant literature but specifics on the chemical-physical nature and behavior of hydrogen ions ($H^+$) are lacking. Filling this knowledge gap may increase understanding of soil acidity. If understanding of the chemical-physical nature and behavior of $H^+$ can be increased, then perspective of soil acidity may be broadened.  The objective of this review is to describe the chemical-physical nature and behavior of $H^+$.  The objective is augmented by recapping the concept of acidity, explaining why $H^+$ are acidity, identifying sources of $H^+$ contributing to acidity, examining water's role in $H^+$ behavior, and evaluating the link between $H^+$ and aluminum ($Al^{3+}$). Physically, $H^+$ are protons, composite particles comprised of quarks bound together by gluons; hydrogen nuclei absent neutrons and electrons ($e^-$).  Due to $e^-$ deficiency and high charge density, $H^+$ polarize the orbital $e^-$ distribution of hydroxyl anion ($OH^-$) explaining dissolution of hydroxy-Al minerals like gibbsite ($\gamma$-Al(OH)$_3$) at low pH releasing $Al^{3+}$ to soil solution.  Solution $Al^{3+}$ induces plant stress and nutrient imbalance via oxidative effects on roots and impacts on CEC.  Both $H^+$ and $Al^{3+}$ are Lewis-acids.  Understanding the Lewis-acid behavior of $H^+$ and $Al^{3+}$ helps explain the nature of acidity and its effects on plants and soils. Describing the chemical-physical nature and behavior of $H^+$ helps shape the evolution of thinking about intrinsic soil characteristics like pH, which is a goal of plant and soil sciences.*

## Introduction

Soil in humid regions may be naturally acidic or may turn acidic with agricultural use (Bear, 1957). Soil with pH < 5.5 represent 30% to 50% of arable land (Aggarwal et al., 2015; Rahman et al., 2018).  At sufficient levels acidity may impact turfgrass quality, or the quality of other plant systems, by stressing or damaging root systems due to the presence of toxic ions and reduced availability of nutrients (Carrow et al., 2001; Delhaize and Ryan, 1995; Foy, 1992; McCarty et al., 2003).  Root stress or root damage resulting from soil acidity may result in the thinning, stunting, and chlorosis of turfgrass shoots (Fig. 1) and visible necrosis of plant roots (Fig. 2).



**Figure 1:** Chlorosis and thinning of a Tifway 419 hybrid bermudagrass [*Cynodon dactylon* (L.) Pers. x *Cynodon transvaalensis* Burtt-Davy] fairway in response to soil with pH < 4.0 at the 5 cm depth in west central Florida.  Replacement of injured 419 with sod was required to improve turfgrass quality, but ultimately the new sod also failed.  Treatment with dolomitic limestone corrected the problem and improved turfgrass quality.  Photo by W. Berndt.

**Figure 2.** Root discoloration and necrosis of a goosegrass [*Eleusine indica* (L.) Gaertn.] plant growing in a Tifway 419 hybrid bermudagrass fairway (Fig. 1) in response to soil with pH < 4.0 at the 5 cm depth in west central Florida. Photo by W. Berndt.

Soil acidity and its effects have been reported in the literature for over 100 years (Callahan et al., 1998; Cox, 1929; Guertal and McElroy, 2018; Hartwell and Damon, 1917; Johnson, 1951; Lundberg et al.,1977; Musser, 1962; Oakley, 1925; Potter et al., 1985; Sartain, 1985; Schmid et al., 2017; Smiley and Craven, 1978; USGA Green Section, 1925a; USGA Green Section, 1925b; USGA Green Section, 1926; Westover, 1925). Description and measurement of hydrogen ion (H$^+$) activity as pH has been addressed (Bloom et al., 2005; Bohn et al., 1979; Carrow et al., 2001; Foth and Ellis, 1997; Lindsay, 1979; McCarty et al., 2003; Sposito, 2008; Tisdale et al 1985; Turgeon, 2008) and information on liming to mitigate excess acidity is available on the internet (Table 1), as well as in turfgrass textbooks (Carrow et al., 2001; McCarty et al., 2003; Turgeon, 2008) or texts on soil fertility (Foth and Ellis, 1997; Tisdale et al., 1985).

| Table 1. Partial listing of internet resources for evaluating total neutralizing power (TNP) of liming materials. | |
| --- | --- |
| Organization | URL |
| Cornell University Cooperative Extension | Factsheet#7.doc (cceonondaga.org) |
| University of Nebraska Lincoln | extensionpublications.unl.edu/. |
| A&L Laboratories Canada, Inc. | Choosing a Liming Material \| A&L Fact Sheet 522 |
| University of Wisconsin Extension | Choosing Liming Materials (A3671) (wisc.edu) |
| United States Department of Agriculture | Liming to Improve Soil quality (usda.gov) |
| North Carolina State University Extension | Soil Acidity and Liming (ncsu.edu) |

What is lacking in the literature is concise explanation of what H$^+$ are chemically and physically and how or why H$^+$ behave as they do. Filling this knowledge gap may increase understanding of soil acidity. If understanding of the chemical-physical nature and behavior of H$^+$ can be increased, then perspective of soil acidity may be broadened. Broadening the perspective of soil acidity is desirable because shaping the evolution of thinking about intrinsic soil characteristics like pH is a goal of plant and soil sciences. The objective of this review is to describe the chemical-physical nature and behavior of H$^+$, and is augmented by recapping the concept and origin of acidity, explaining why H$^+$ are considered acidity, identifying sources of H$^+$ contributing to acidity, examining the role of water in H$^+$ behavior, and evaluating the link between H$^+$ and aluminum (Al$^{3+}$). The relationship between excess H$^+$ and the occurrence of toxic ions and their effects on plants and inducement of nutrient deficiencies is also reviewed.

**A Taste of Acidity**

The term acidity dates to the 8$^{th}$ century conveying the sour taste of foods or beverages (Chang et al 2010; Chang, 2012; Lowrey, 1915; Olah et al., 2009; Ruthenberg and Chang, 2017; Tu et al., 2018). One conspicuous property of acids is sour taste (Chang et al, 2010; Lowrey, 1915; Tu et al., 2018). Sour is one of five basic taste sensations (Sour: Merriam-Webster) and is associated only with acids (Neta et al., 2007). Sourness is rated relative to dilute hydrochloric acid (HCl) that has a sourness index (SI) of 1.0 (Pattarapon et al., 2017; Rizzolo and Cortellino, 2018) By comparison, the SI for tartaric acid (C$_6$H$_6$O$_6$) = 0.7, for citric acid (C$_6$H$_8$O$_7$) SI = 0.46, and for carbonic acid (CH$_2$O$_3$) SI = 0.06 (Pattarapon et al., 2017).

*Oxygen Theory*. In 1772-1780 Antoine Lavoisier theorized that oxygen (O) was the acidic moiety, the principle of acidity, because at the time acids were thought to consist of respirable air (Chang 2012; Crosland, 1973; Khun, 1962; Lavosier, 1806; Pearson, 1792). This reflected knowledge of oxoacids including nitric acid (HNO$_3$). In 1779 Lavoisier created the word oxygen from the Greek *oxys* meaning sour, sharp, or acid (Crosland, 1973). *Oxys* is one of the first words coined to mean principle of acidity (Crosland, 1973). The words acid and acetic (i.e., acetic acid, C$_2$H$_4$O$_2$) are from the Latin *acere* meaning sour (Lowrey,

1915; Ruthenberg and Chang, 2017). The term sour soil was used in early turfgrass writings (Barron, 1906; Carrier, 1924; Piper and Oakley, 1921a; Piper and Oakley, 1921b) being synonymous with acid soil (USGA Green Section, 1925a; Wherry, 1920).

*Electrolytic Theory.* The link to acidity and O was eventually rejected because it was shown HCl and certain other acids did not contain O (Bell, 1973; Chang, 2012; Davy, 1810; Weller, 1999). In the late 19th century Svante Arrhenius linked acidity to $H^+$ through experiments involving electrolytic dissociation of $H_2O$ (Eq. 1) yielding $H^+$ and hydroxyl anion ($OH^-$) (Chang, 2012; Olah

$$H_2O \leftrightarrow H^+ + OH^- \qquad \text{Eq. 1}$$

et al., 2009). By making conductance measurements on pure $H_2O$ Arrhenius deduced that spontaneous dissociation of $H_2O$ produced equal numbers of $H^+$ and $OH^-$ ions (electrolytes) that were responsible for conducting current. This research ultimately led Arrhenius, based on additional conductance measurements (Arrhenius, 1887; Arrhenius 1903), to identify acidity with the ability of substances that contain hydrogen (i.e., HCl) to produce excess $H^+$ when dissolved in aqueous solution (Chang, 2012; Munjal and Singh, 2019; Olah et al., 2009). As a result, acids were defined as hydrogen compounds that dissociate in $H_2O$ producing excess levels of $H^+$; bases dissociate in $H_2O$ to give excess $OH^-$. The Arrhenius theory of acidity appears to be the oldest acid-base model. It is sometimes referred to as the water model of acidity because $H_2O$ is the solvent. Alternatively, the Arrhenius theory is also termed the electrolytic theory of acidity because it is based on ionization of H substances in $H_2O$ (Cherginets, 2005).

*Proton Theory.* In 1923 J.N. Bronsted and T.M Lowry further defined acids as species that donate $H^+$ and bases as species that accept $H^+$ regardless of solvent nature (Bak, 1974; Flowers et al., 2019; Olah et al., 2009). In the Bronsted-Lowry theory of acidity ionization of acid (HA) in solvent (S) produced a new acid $SH^+$ and base $A^-$ (Eq. 2). The acid-base pair that differs by a $H^+$ is referred to as the conjugate acid-base pair. Acids can lose $H^+$ to become conjugate bases and bases accept $H^+$ to become conjugate acids. The Bronsted-Lowry theory of acidity is also called the proton theory of acidity (Munjal and Singh, 2020) and focuses on $H^+$ transfer between species but fails to account for reactions in which no $H^+$ is transferred (Flowers et al., 2019).

$$HA + S \leftrightarrow A^- + SH^+ \qquad \text{Eq. 2}$$

*Electronic Theory.* At about the same time, G.N. Lewis proposed that acids, based on electronic structure, and referred to as Lewis-acids, are substances that accept electrons ($e^-$) from Lewis bases forming a shared $e^-$ pair bond resulting in formation of a Lewis acid-base adduct (Atkins et al., 2010; Calvin, 1982; Flowers et al., 2019; Lewis, 1923). Lewis theory represented a different way of viewing acid-base reactions expanding the scope of what acids are ( Lewis Acids and Bases(purdue.edu)). Lewis theory focused not on $H^+$ transfer to a base but rather on $e^-$ transfer from a base. As an example, $H^+$ is a Lewis-acid because it accepts an $e^-$ pair from the Lewis-base ammonia ($NH_3$) (Fig. 3). The Lewis theory of acidity is called the electronic theory of acidity (Cherginets, 2005).
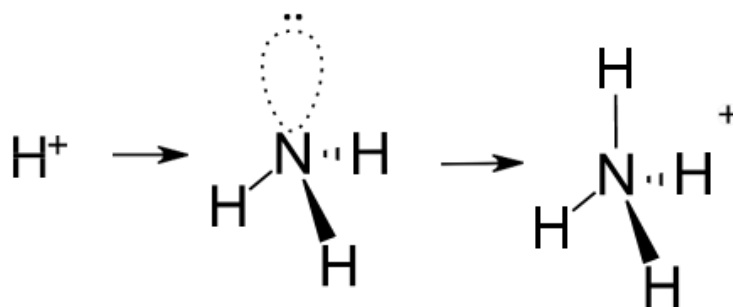


**Figure 3.** Formation of ammonium ion ($NH_4^+$) is a Lewis acid-base reaction. Protonation of the Lewis-based $NH_3$ forms the Lewis acid-base adduct $NH_4^+$. In this reaction $H^+$ is an $e^-$ deficient Lewis-acid forming a dative or coordinate-covalent bond with the unsatisfied $e^-$ pair of the N atom in the $NH_3$ (Atkins et al., 2010). The $NH_3$ is an $e^-$ pair donor or nucleophile and $H^+$ is an $e^-$ pair acceptor or electrophile. As a result of its affinity for $e^-$ the $H^+$ physically pulls the unsatisfied $e^-$ pair of the $NH_3$-N forming a bond and changing its molecular geometry from triagonal pyramidal to tetrahedral.

Lewis theory explains Bronstead-Lowry theory in terms of electronic structure (Flowers et al., 2019) and offers a broader view of acids and bases (McCarty et al., 2003). The transfer of $e^-$ charge from nucleophile ($NH_3$) to electrophile ($H^+$) forms a dative (coordinate-covalent) bond (Lewis, 1923). Dative bonds form when $e^-$ pairs come from one nucleophilic atom participating in the reaction (i.e., the N in $NH_3$). Lewis-acids are $e^-$ deficient cations including $H^+$, aluminum ($Al^{3+}$), and other cations and molecules common to plant-soil systems. Dissociation of hydrogen compounds like HCl in solution releasing $e^-$ deficient Lewis acids (i.e., $H^+$) that

seek available $e^-$ from donors is a fundamental concept in acidity, with $H^+$ being the acidic character.

**Hydrogen Ions Are Particles**

Hydrogen ions are referred to as protons (Bloom et al., 2005; Coleman and Mehlich, 1957; Connelly et al., 2005; McClean, 1982; Olah et al., 2009; Sposito, 2008) because that's what they physically are. Discovery of the proton as a nuclear constituent is attributed to Ernest Rutherford resulting from experimentation involving collisions of high energy $\alpha$-particles with nitrogen (N) nuclei (Longair, 2021; Rutherford, 1919).

The collisions of α-particles with N liberated positively charged hydrogen ($H^+$) nuclei subsequently referred to as protons (Chadwick, 1932).

Protons are composite, sub-atomic particles consisting of quarks held together by gluons via strong interaction dynamics (Lin et al., 2022; Ling et al., 2021; Sahoo and Nayak, 2022). Hydrogen (H) is also reported to be distributed as a wave function making protons quantum objects (Fang et al., 2019). Quarks and gluons are elementary particles considered fundamental constituents of matter that combine to become composite particles. The physical arrangement of quarks as protons consists of two up quarks (u quarks) and one down quark (d quark) as a triquark arrangement (Table 2) mediated by gluons via the strong interaction (Ling et al., 2021); gluons are strong force carriers (i.e., color force carriers) referred to as gauge bosons that act to confine assembly of quarks as particles. The strong interaction is one of four fundamental forces of nature, along with electromagnetism, the weak nuclear force, and gravity; all four forces appear to play a role in quark-gluon behavior (Ling et al., 2021). The strong force acts over short distances of $10^{-15}$ m. The color force may be responsible for strong interaction dynamics and confinement of quarks (Color Force (gsu.edu)). The property of quark color plays the same role in the strong force that charge does in electromagnetic interactions (Ling et al., 2021).

Protons are hadrons, particles having two or more quarks (Hadrons (gsu.edu)). Protons are further classified as baryons having odd numbers of quarks. Baryons and quarks are referred to as fermions (Ling et al., 2021), which are particles following Fermi-Dirac statistics and obeying the Pauli exclusion principle. Fermi-Dirac statistics describe the energy distribution of fermions (Biswas, 2014). The Pauli exclusion principle says no two fermions can exist in identical quantum energy states at a given time (Kaplan, 2022; Ling et al., 2021). The color force may be a workaround to explain two up quarks existing simultaneously within the proton's boundary although a definite proton boundary possibly visualized as a sphere with a physical perimeter does not exist. Baryons are associated with matter. Alternatively, bosons like gluons follow Bose- Einstein statistics, which says an unlimited number of gluons can condense into the same energy level; bosons are considered strong force (color force) carriers. Gluons are exchange particles for the color force between quarks (Exchange Particles (gsu.edu)). Fermions and bosons represent two separate families of particles.

## Particles Formed with the Big Bang

Protons probably originated with cooling of the quark-gluon plasma (QGP), a hot, dense primordial soup of deconfined quarks and gluons and other particles that formed 13.8 billion years ago with the big bang (Ling et al., 2021; Sahoo and Nayak, 2022). Plasma is a fundamental highly oxidized state of matter containing charged particles and often called the fourth state of matter (MIT Plasma Science). Cooling of QGP began microseconds after $t = 0$ (i.e., the singularity) probably at Planck time ($t_p$, $10^{-43}$ sec) to temperature less than Planck scale, which is $10^{32}$ kelvins (K), mitigating deconfinement of quarks and gluons ultimately leading to formation of various particles with the expansion and continued cooling of the universe (Chapter 2 (umd.edu)). The strong force probably began at $10^{-35}$ sec after $t_p$ when the temperature of the universe was $10^{27}$ K (Ling et al., 2021). In theoretical particle physics quantum chromodynamics (QCD), which is the theory of the strong-color force, predicts confinement of partons (quarks and gluons) inside the cage (bound state) of hadrons (protons) (Sahoo and Nayak, 2022).

| Table 2. Physical properties of quarks (Ling et al., 2021). All quarks are spin-half fermions with fractional charge. Protons consist of two up quarks and one down quark giving quantum charge of +1 ($+4/3 - 1/3 = +1$). | | | |
|---|---|---|---|
| Quark Type | Charge† | Spin‡ | Baryon¶ |
| Down | −1/3 | 1/2 | 1/3 |
| Up | +2/3 | 1/2 | 1/3 |
| †Charge quantum number. | | | |
| ‡Quantum angular momentum. | | | |
| ¶Additive quantum number. | | | |

*Hydrogen Isotopes.* The hydrogen atom is the simplest atom in nature (Ling et al., 2021) and is the most abundant element in the universe. The most common isotope of atomic hydrogen is protium (> 99.98%), consisting of one proton and one $e^-$ and denoted $^1H$. The superscript 1 on $^1H$ is the mass number designating the sum of protons plus neutrons. Protium is electrically neutral (stable) having a half-life on the order of $10^{36}$ years (Isotopes of Hydrogen (arizona.edu)). Cationic $^1H^+$ are oxidized protium; unstable bare positively charged hydrogen nuclei absent neutrons or $e^-$ (Bahl et al., 2010; Bell, 1973; Olah et al., 2009; Stewart, 1985) (Eq. 3).

$$^1H \rightarrow {}^1H^+ + e^- \qquad \text{Eq. 3}$$
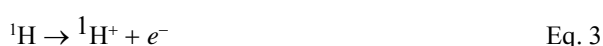
The energy required to remove the $e^-$ from the $1s$ orbital of $^1H$ is $\approx 2.2^{-18}$ J or 13.6 electron volts (eV) (Kramida et al., 2021). This energy is sufficient to overcome the Coulomb (electrostatic) force holding atomic hydrogen ($^1H$) together. An example of the oxidation of atomic hydrogen producing $H^+$ occurs during nitrification (Eq. 4) mediated by *Nitrosomonas* and similar bacteria. The reaction in Eq. 4 is catalyzed by a series of enzymes including ammonia monooxygenase and hydroxylamine oxidoreductase.

$$NH_3 + O_2 \rightarrow NO_2{}^- + 3\,H^+ + 2\,e^- \qquad \text{Eq. 4}$$
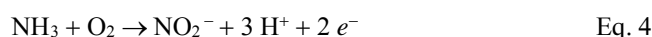
**Hydrogen Ions are Small**

Cationic $^1H^+$ are $10^5$ or more times smaller than any other cation with a radius ($r$) on the order of $1^{-14}$ m (Bell, 1973; Olah et al., 2009). More recently, Kharzeev (2021) reported the root mean square charge radius of gas phase $H^+$ was $8.41^{-16}$ m. All other cations have an associated $e^-$ cloud composed of one or more orbital $e^-$ increasing ionic $r$. For perspective, the $r$ for atomic $^1H$ with its single orbiting $1s$ $e^- \approx 3^{-11}$ m; $r$ for $^1H^+$ is $\approx 10^5$ times smaller. Using Kharzeev's value for $r$ the calculated spherical volume (V) of $^1H^+$ is $\approx 2.5^{-45}$ m$^3$ versus $\approx 1^{-31}$ m$^3$ for $^1H$. The $r$ for $Al^{3+}$ is $5.35^{-11}$ m (Haung et al., 2013) and calculated V = $6.4^{-31}$ m$^3$.

*Charge Density.* Protons have a net positive charge of $+1e$ where $e = +1.6$ x $10^{-19}$ Coulombs (Bahl et al., 2010; Flowers et al., 2019). Due to small ionic volume and high charge density, meaning the positive charge is concentrated in a small volume, $H^+$ are highly reactive and have a polarizing effect on other substances (Bell, 1973; Olah et al., 2009; Sposito, 2008); unstable $H^+$ react with orbital $e^-$ from anions to form bonds to confer electronic stability. Polarization refers to the relative ability of a cation to distort the geometry of the $e^-$ cloud (charge distribution) of a bond with an anion. Electronic distortion effected by the polarizing power of $H^+$ when pH is low affects bond strength and stability of exposed substances leading to effects on material properties such as solubility (Fig. 4).
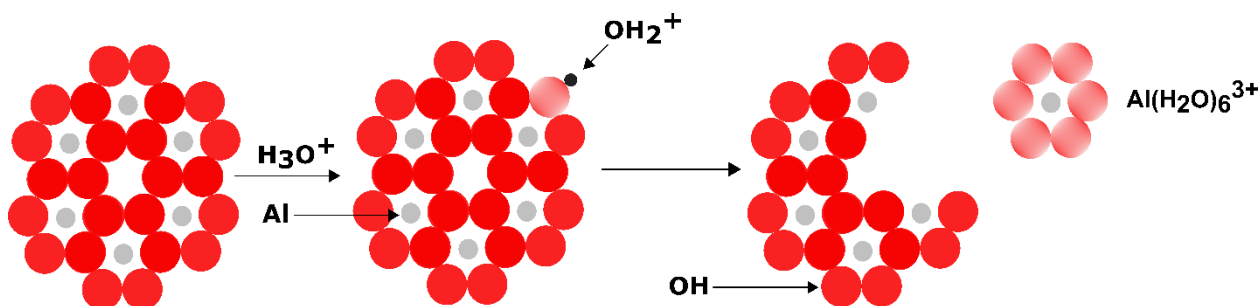


**Figure 4.** Proton attack of gibbsite ($\gamma$-Al (OH)$_3$) at pH < 5.5 leading to release of aluminum ion ($Al^{3+}$, gray dot) to soil solution is a two-step process (from Sposito, 2008). Dissolution begins with $H^+$ adsorption (protonation, black dot) to an edge hydroxyl anion (OH$^-$, red dot) forming OH$_2^+$ eventually disrupting mineral arrangement (i.e., internal bonds between OH$^-$ and $Al^{3+}$). The OH$^-$ is a Lewis-base or ligand (i.e., binding species). With time, bonds with the metal-anion near the site of $H^+$ adsorption weaken and fail, and the metal-anion complex eventually detaches forming a solvation complex Al (H$_2$O)$_6^{3+}$ (i.e., free $Al^{3+}$), which is an octahedral coordination complex between $Al^{3+}$ and H$_2$O. Hydronium (H$_3$O$^+$) is hydrated $H^+$.

The rate of dissolution for soil minerals (i.e., clays, metal oxides) is surface controlled following zero-order kinetics (Sposito, 2008). The zero-order kinetic model describing the surface-controlled rate of dissolution is given as Eq. 5:
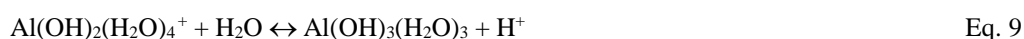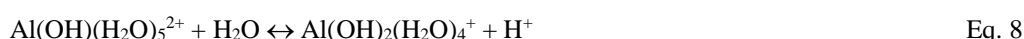
$$d[A]/dt = -kd \qquad \text{Eq. 5}$$

On integration this becomes Eq. 6:

$$A_t = A_0 - kt \qquad \text{Eq. 6}$$

where $A_t$ is the concentration of substrate (i.e., aqueous-phase $[Al^{3+}]$) remaining at any time ($t$), $A_0$ is the initial concentration of substrate (i.e., the $y$-intercept), $k$ is the rate constant (i.e., concentration time$^{-1}$), $A_0 \div 2k$ is the half-life ($t_{1/2}$), and $A_0 \div k$ is the mean residence time ($t_{mrt}$) or turnover time (Paul and Clark, 1997; Sposito, 2008). The rate constant ($k$) is independent of $A_0$ but depends on temperature, pressure, and $[H^+]$ (Sposito, 2008).

Aluminum ion ($Al^{3+}$) is also highly polarizing, which helps explain hydrolysis of Al(H$_2$O)$_6^{3+}$ releasing $H^+$ to solution generating additional acidity (Eq. 7-10). The high charge density and small ionic radius of $Al^{3+}$ leads to polarization of adsorbed H$_2$O of Al(H$_2$O)$_6^{3+}$ peeling off $H^+$ in successive steps. The successive release of $H^+$ is part of the reason Al has been called the seat of soil acidity (Jenny, 1961); the physical nature of $Al^{3+}$ as an $e^-$ deficient Lewis-acid has a profound impact on the coordinate bonds of H$_2$O adsorbed to the $Al^{3+}$. The $Al^{3+}$ distorts O–H bond geometry making bonds weaker resulting in release of $H^+$ to solution; $Al^{3+}$ polarizes the H$_2$O surrounding it. In this case H$_2$O is a Lewis-base or ligand (Atkins et al., 2017). The $H^+$ that are released may further react to dissolve minerals releasing still more $H^+$ (Foth and Ellis, 1997; Tisdale et al, 1985) potentially developing acid soil with time.

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow Al(OH)(H_2O)_5^{2+} + H^+ \qquad \text{Eq. 7}$$

$$Al(OH)(H_2O)_5^{2+} + H_2O \leftrightarrow Al(OH)_2(H_2O)_4^+ + H^+ \qquad \text{Eq. 8}$$

$$Al(OH)_2(H_2O)_4^+ + H_2O \leftrightarrow Al(OH)_3(H_2O)_3 + H^+ \qquad \text{Eq. 9}$$

$$Al(OH)_3(H_2O)_3 + H_2O \leftrightarrow Al(OH)_4(H_2O)_2^- + H^+ \qquad \text{Eq. 10}$$

*Lewis Acids.* Protons and common soil metals (Table 3) are Lewis-acids forming bonds with

Table 3. Comparison of spherical volume charge (PV) calculated for cations common to plant-soil systems. For isolated H+ (gas phase) an ionic radius of $8.41^{-16}$ m was taken from Kharkzeev et al. (2021). Radius values for other cations were adapted from Huang et al. (2013). Volume charge was calculated using the elementary charge (e or q) of $1.602^{-19}$ coulombs (C) as numerator ($P_V = q/V$). The $P_V$ for $H^+$ and thus its polarizing power, is orders of magnitude greater than for other cations.

| Cation | Ionic Radius (m) | Spherical Volume (m$^3$) | $P$ (C m$^{-3}$)† |
|---|---|---|---|
| $H^+$ | $8.41^{-16}$ | $2.5^{-45}$ | $6.4^{28}$ |
| $Al^{3+}$ | $5.35^{-11}$ | $6.4^{-31}$ | $7.5^{11}$ |
| $Fe^{3+}$ | $5.50^{-11}$ | $7.0^{-31}$ | $6.9^{11}$ |
| $Fe^{2+}$ | $7.40^{-11}$ | $1.7^{-30}$ | $1.9^{11}$ |
| $Mn^{2+}$ | $8.00^{-11}$ | $2.1^{-30}$ | $1.5^{11}$ |
| $Mg^{2+}$ | $6.60^{-11}$ | $1.2^{-30}$ | $2.6^{11}$ |
| $K^+$ | $1.33^{-10}$ | $9.9^{-30}$ | $1.6^{10}$ |
| † Volume charge in Coulombs (C) m$^{-3}$. | | | |

substances having unshared $e^-$ pairs (Atkins et al., 2010; Bahl et al., 2010; Olah et al., 2009; Sposito, 2008). Due to extreme $e^-$ affinity, resulting from small size and large charge density, $H^+$ have no independent existence in the condensed state always being bound by $e^-$ from another atom (Stewart, 1985). As a result of its Lewis-acid behavior $H^+$ bind with $H_2O$ in aqueous solutions to give $H_3O^+$ (Fig. 5) or it binds to other available Lewis-bases like $NH_3$. The turfgrass literature
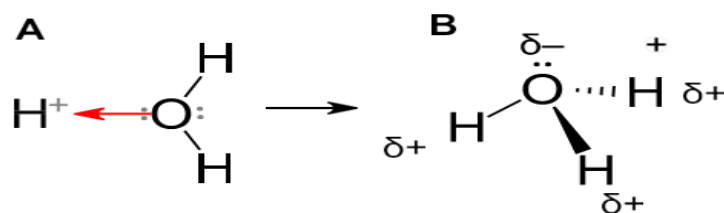


**Figure 5.** Protonation of $H_2O$ forming $H_3O^+$ in aqueous environments is a Lewis acid-base reaction. The $H_3O^+$ is a Lewis acid-base adduct. A: the red arrow indicates movement of an $e^-$ pair from the O atom towards $H^+$ forming a dative bond. Movement of the $e^-$ pair, in effect $e^-$ distortion, is a result of attraction exerted by $H^+$ due to its large positive charge density. B: for isolated $H_3O^+$ the partial charge on the O atom is $-0.82e$ while each H is $+0.61e$ (www2.chem.wisc.edu) with sum = $+1e$. Formation of $H_3O^+$ is the first step in formation of protonated water clusters (PWC) with configuration of $H_3O^+(H_2O)_n$.

(McCarty et al., 2001) and other plant-soil literature may use the term free $H^+$ in addressing measurement of soil pH but free $H^+$ exists only in a vacuum or dilute gas (Bell, 1973).

## Hydronium Solvation

Once $H_3O^+$ is formed it immediately establishes hydrogen bonds (H-bonds) with $H_2O$ producing protonated water clusters or PWC (Fig. 6). When $H_3O^+$ forms H-bonds with three $H_2O$ molecules, forming its first solvation shell, the structure is called the Eigen cation ($H_9O_4^+$) (Amir et al., 2007; Kulig and Agmon, 2013; Swanson and Simons, 2009). Eigen is an idealized form of solvated excess $H_3O^+$ and may be the most prevalent liquid phase water structure assuming a central role in acidic solutions (Atkins et al., 2010; Agmon et al., 2016; Kulig and Agmon, 2013) although there are different PWC isomers of the form $H_3O^+(H_2O)n$. Atkins et al. (2010) suggests a cage of $H_2O$ molecules condense around $H_3O^+$ in a pentagonal dodecahedral arrangement with the structure $H_3O^+(H_2O)_{21}$. Shi et al. (2018) describes PWC isomers as chain-like ($H_3O^+(H_2O)_{2-9}$) or cage-like ($H_3O^+(H_2O)_{10-17}$).
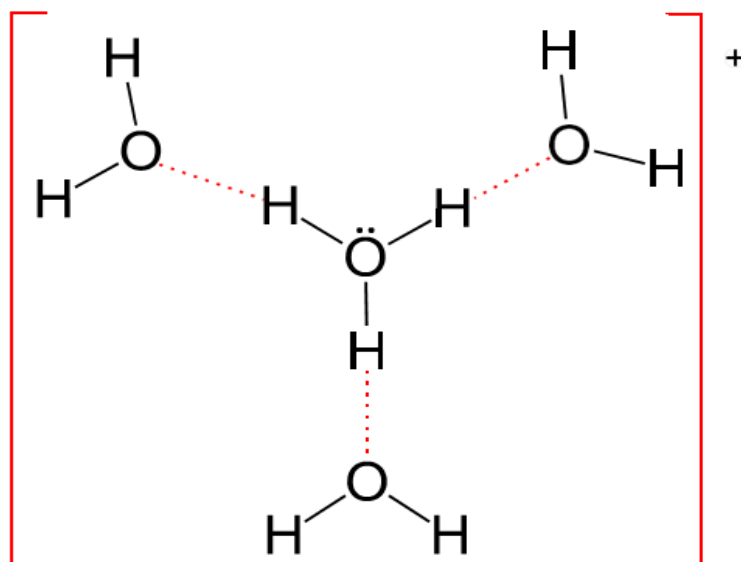
**Figure 6.** Two-dimensional structure of the protonated water cluster (PWC) Eigen cation ($H_9O_4^+$). The basis of this PWC centers on $H_3O^+$ attached to three $H_2O$ via hydrogen bonds (dotted lines). Hydrogen bond lengths for Eigen in the first solvation shell $\approx 1.5^{-10}$ m (Agmon, 1995; Chaudhari and Lee, 2010; Schran and Marx, 2019). The three $O_9$-$O_4$ distances are $\approx 2.6^{-10}$ m.

**The Hydrogen Bond Wired Network**

The movement of $H^+$ to and from substances in aqueous solutions is the heart of acidity (Bell, 1936; Bell and Lidwell, 1940; Rini et al., 2003; Stewart, 1985). To illustrate, autoionization of water (Eq. 11) is spontaneous movement of $H^+$ from one $H_2O$ to another forming $H_3O^+$ (Atkins, et al., 2010; Bahl et al., 2010; Flowers et al., 2019; Stewart, 1985). Autoionization of $H_2O$ is temperature dependent given by the ionization constant $K_w$ (Table 4).
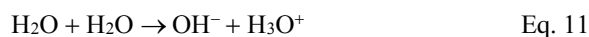
$$H_2O + H_2O \rightarrow OH^- + H_3O^+ \qquad \text{Eq. 11}$$

Table 4. Ionization constants ($K_w$) for pure water for various temperatures from engineeringtoolbox.com. Molar ($M$) concentration of hydrogen ions $[H^+] = \text{SQRT}(K_w)$. Tabled pH was calculated as $-\log_{10}[H^+]$. Each pH value is neutral with $[H_3O^+] = [OH^-]$ for that temperature.

| Temperature (°C) | $K_w$ | $pK_w$† | pH | $[H_3O^+]$ |
|---|---|---|---|---|
| 0 | $0.114 \times 10^{-14}$ | 14.943 | 7.472 | $3.376 \times 10^{-8}$ |
| 10 | $0.292 \times 10^{-14}$ | 14.534 | 7.267 | $5.404 \times 10^{-8}$ |
| 25 | $1.012 \times 10^{-14}$ | 13.996 | 6.997 | $1.006 \times 10^{-7}$ |
| 38 | $2.523 \times 10^{-14}$ | 13.598 | 6.799 | $1.588 \times 10^{-7}$ |
| 50 | $5.470 \times 10^{-14}$ | 13.262 | 6.631 | $2.339 \times 10^{-7}$ |
| 66 | $12.735 \times 10^{-14}$ | 12.895 | 6.448 | $3.569 \times 10^{-7}$ |
| 93 | $43.652 \times 10^{-14}$ | 12.360 | 6.180 | $6.607 \times 10^{-7}$ |
| 100 | $55.976 \times 10^{-14}$ | 12.252 | 6.126 | $7.482 \times 10^{-7}$ |
| †$pK_w = -\log_{10}K_w$. | | | | |

In pure $H_2O$ at 25°C only 6 of $10^8$ $H_2O$ molecules spontaneously dissociate to produce equal quantities of $OH^-$ and $H_3O^+$ with pH being neutral (Flowers et al., 2019).

*Spontaneous Dissociation.* Autoionization of water begins when a voltage fluctuation in the electric field of $H_2O$ results in cleavage of an O–H bond on a $H_2O$ molecule (Chandler et al., 2012; Geissler et al., 2001; Hassanali et al., 2011). Electric field fluctuations in $H_2O$ are due in part to liberational motions of dipoles (Geissler et al., 2001). Water is dipolar (i.e., it has a dipole moment) having both positive (+) and negative (−) charges associated with the molecule separated by physical distance and due to differences in electronegativity between O and H (Flowers et al., 2019). The dipole moment of $H_2O$ plays a role in formation of H-bonds with other molecules, which facilitates $H^+$ movement.

*Grotthuss Mechanics.* When auto-dissociation occurs the transient $H^+$ from one $H_2O$ is transported to another $H_2O$ molecule by the Grotthuss mechanism forming $H_3O^+$ within $\approx 3^{-14}$ sec (Chandler et al., 2012; Geissler et al., 2001; Rini et al., 2003). Proton movement via Grotthuss mechanics is sometimes referred to as $H^+$ jumping or hopping within the framework of an H-bond network (Hammes-Schiffer, 2021); H-bonds constitute the framework. Hydrogen bonds are primarily electrostatic intermolecular attractive forces linking the O in one $H_2O$ to an H in another (Fig. 7) (Chaplin, 2007; Flowers et al., 2019). Water may be analogous to a fabric of $H_2O$ molecules. Linked together by a network of H-bonds that serve as conductors for $H^+$ and $OH^-$ movement; a three-dimensional wire system linking individual $H_2O$ molecules together as a wired network (Chandler et al., 2012; Geissler et al., 2001). Both $H^+$ and $OH^-$ are conducted across the H-bond wire path. When this movement occurs a $H_2O$ transiently becomes $H_3O^+$ while another becomes $OH^-$ (Geissler et al., 2001). If the H-bond network remains intact there is probability the ions will recombine reforming the original $H_2O$ (Hassanali et al., 2011). If the H-bond wire fabric reorients then PWC may form, and the system transiently remains in the charge-separated state. One picosecond ($10^{-11}$ sec) is consistent with the rate H-bonds reorient (Geissler et al., 2001).
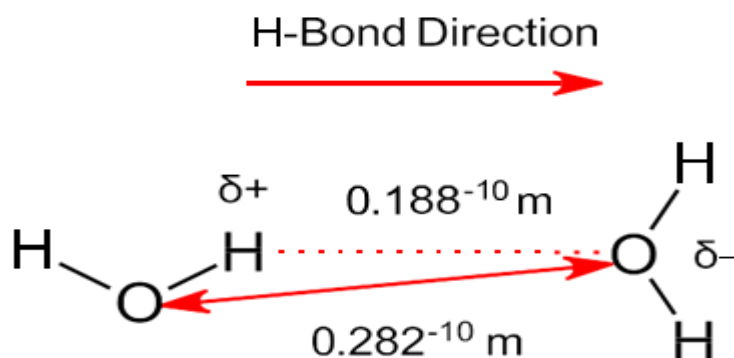


**Figure 7.** Hydrogen bond (H-bond, dotted red line) parameters in liquid $H_2O$ (from Chaplin, 2007). The $H_2O$ (left) is the H-bond doner and the $H_2O$ (right) is the H-bond acceptor. The partial charge on O averages $\approx -0.7e$ and the partial charge on H $\approx +0.35e$. Bond length between $H_2O$ molecules averages $\approx 0.188^{-10}$ m increasing with temperature. Distance between O atoms (solid red line) is $\approx 0.282^{-10}$ m. Hydrogen bond strength decreases from about 23 kJ mol$^{-1}$ for liquid $H_2O$ at 0°C to about 17 kJ mol$^{-1}$ in liquid $H_2O$ under pressure at 200 C°

Soil solution is not pure $H_2O$, it is an open $H_2O$ system (Lindsay, 1979; Sposito, 2008) containing a variety of mineral and organic constituents. Thus, $H^+$ movement in soil solution may be more complex but the principle remains. An influx of $H^+$ into soil increases the level of acidity (i.e., greater concentrations of PWC) and influx of $OH^-$ decreases it.

## Sources of $H^+$ to Soil

Hydrogen ions in soil originate from biogeochemical reactions of minerals and organic matter and from natural and anthropogenic inputs (Jenny, 1961; McCarty *et al.*, 2003; Sposito, 2008; Tisdale et al., 1985; Thomas and Hargrove, 1984; Thomas, 1996). Wetfall (rain, snow), dryfall (deposited solid particles) and interflow (movement of soil water) carry $H^+$ into soil solution from external sources (Sposito, 2008) where $H^+$ remains in motion on the H-bond wire network as active acidity (intensity) or transiently adsorbed by cation exchange sites as exchangeable acidity (capacity).

*Natural Inputs.* Atmospheric $CO_2$ and soil respiration are sources of $H^+$ to soil (Sposito, 2008). Carbon dioxide diffuses into and through soil dissolving into soil solution producing carbonic acid ($H_2CO_3$), and bicarbonate ($HCO_3^-$) releasing $H^+$ (Eq. 12). Diffusion of $CO_2$ into soil is due to the

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad \text{Eq. 12}$$

pressure of the atmosphere. Soil generated $CO_2$ is due to root respiration and microbial respiration during mineralization of soil organic matter (SOM). Mineralization of SOM ultimately yields humus, with annual $CO_2$ emissions an order of magnitude greater than fossil fuel combustion (Sposito, 2008). The mathematical relationship with respect to $CO_2$ and soil pH is given by Eq. 13, where the partial pressure of $CO_2$ (in Pascals) and activity of $HCO_3^-$

$$\frac{P_{co2}}{(H^+)(HCO_3^-)} = 10^{7.8} \qquad \text{Eq. 13}$$

determine pH (Lindsay, 1979; Sposito, 2008). The higher the partial pressure of $CO_2$ the greater the level of $H^+$ released to solution. In most soils the partial pressure of $CO_2$ is higher than in the atmosphere due to release of $CO_2$ from soil respiration (Lindsay, 1979).

Aliphatic organic acids (i.e., oxalic acid, $C_2H_2O_4$) synthesized in humus can dissociate acidic $H^+$ in the normal range of soil pH (Sposito, 2008). Humus also contributes $H^+$ during its formation (Fig. 8) (Paul and Clark, 1996).
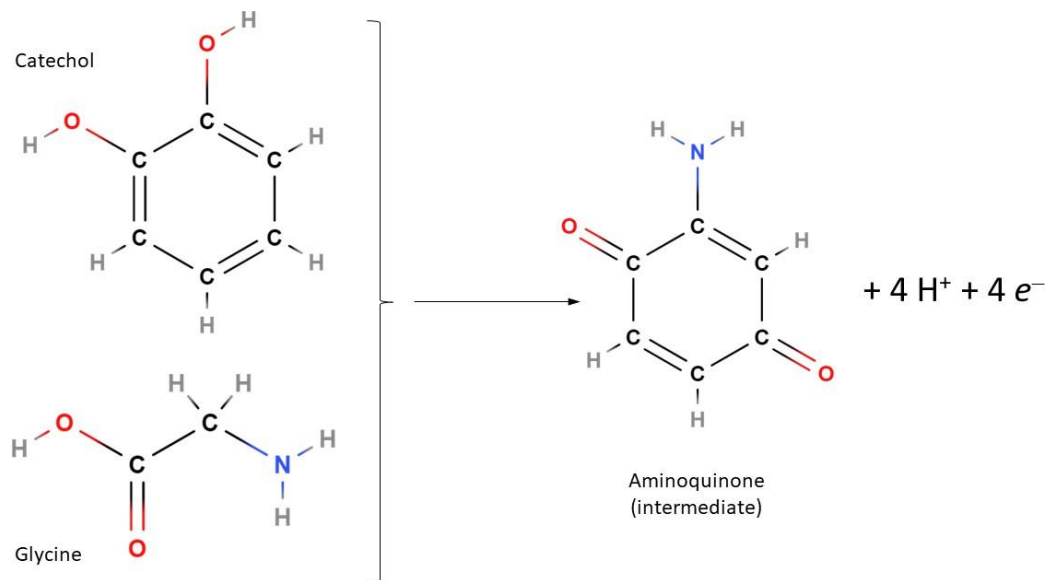


**Figure 8.** Formation of aminoquinone (intermediate) by reacting catechol ($C_6H_6O_2$) and glycine ($C_2H_5NO_2$) during humus formation with release of hydrogen ions ($H^+$) (adapted from Paul and Clark, 1997).

Rainwater and groundwater contribute $H^+$ to soil. The pH of rainwater in equilibrium with atmospheric $CO_2$ is 5.65 (Harter, 2002) but can be 3.5 to 5 (i.e., acid rain) or lower due to anthropogenic inputs (Payus et al., 2020) such as byproducts of the oxidation of fossil fuels. Irrigation water can also be a source of $H^+$. Groundwater used for irrigation in central South Carolina was pH $\approx$ 2-3 causing corrosion and subsequent failure of overhead aluminum irrigation on a seashore paspalum (*Paspalum vaginatum* O. Swartz.) sod field (W. Berndt, personal observation). Leaching soil with excess water can lead to acidification of soil when volume is large and acidic and supplemental fertility does not replace nutrient cations subject to leaching (i.e., $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$). Leaching physically strips soil of basic cations leaving preponderance of $H^+$ in solution or adsorbed to exchange sites.

Plants contribute directly to soil acidity as part of the rhizosphere effect. Roots excrete oxalic acid ($H_2C_2O_4$) and other organic acids (Yang et al., 2019), which dissociate (Eq. 14) releasing

$$H_2C_2O_4 \leftrightarrow HC_2O_4^- + H^+ \qquad \text{Eq. 14}$$

$H^+$. Plants also discharge $H^+$ directly through ion channels in roots (Yang et al., 2019; Zandonadi et al., 2013) counteracting charge imbalance during root uptake of basic cations (Msimbira and Smith, 2020; Sposito, 2008).

Hydrolysis of $Al^{3+}$ and other soil metals can be an important source of $H^+$ (Eq. 4-7). In soils with pH < 5.5 hydrolysis of $Al^{3+}$ and Al-polymers can be a major source of soil acidity (Foth and Ellis, 1997; Lindsay, 1979; Sposito, 2008).

*Anthropogenic Inputs.* Acid-forming fertilizers like ammonium sulfate or $(NH_4)_2SO_4$ contribute $H^+$ due to oxidation of $NH_4^+$ (Eq. 15), which is another Lewis acid. In field research in New Jersey

$$NH_4^+ + 4O_2 \rightarrow 2H_2O + 4H^+ + H_2O \qquad \text{Eq. 15}$$

applying $(NH_4)_2SO_4$ lowered soil pH from 5.45 to 4.98 within two years (Schmid et al., 2017). Using $(NH_4)_2SO_4$ to acidify soil was standard practice for turfgrass management in early years. Repeated applications of acidifying fertilizer (Table 5) almost "miraculously" improved poor, weed-infested turf (Montieth, 1932).

| Table 5. Acidifying fertilizers and acids. | | | | |
|---|---|---|---|---|
| Material | Molecular Formula | Molecular Weight (amu) | Nutrient Percent (%) | Citing Literature |
| Ammonium Nitrate | $H_4N_2O_3$ | 80.04 | N, 35.00 | Mylavarapu et al.,2016; |
| Ammonium Sulfate | $H_8N_2O_4S$ | 132.14 | N, 21.20 | Obear et al., 2016 |
| Ammonium Thiosulfate | $H_8N_2O_3S_2$ | 148.21 | N, 18.90 S, 21.64 | Tisdale et al., 1985; |
| Diammonium Phosphate | $H_9N_2O_4P$ | 132.06 | N, 21.21 P, 23.45 | Tisdale et al., 1985; |
| Ferrous Sulfate | $FeH_{14}O_{11}S$ | 278.02 | Fe, 20.08 S, 11.54 | Mattox et al., 2017; |
| Hydrochloric acid | HCl | 36.46 | n/a | Reid, 1932 |
| Monoammonium Phosphate | $H_6NO_4P$ | 115.03 | N, 12.18 P, 26.93 | Tisdale et al., 1985; |
| Phosphoric Acid | $H_3O_4P$ | 97.99 | P, 31.61 | Carrow et al., 2001; |
| Sulfur | S | 32.07 | S, 100.00 | Mattox et al., 2020; McDonald et al., 2018; |
| Sulfur Coated Urea | $CH_4N_2O$-S | | n/a | Mylavarapu et al., 2016; |
| Sulfuric acid | $H2O4S$ | 98.08 | S, 32.70 | Reid, 1932 |
| Sulfurous acid | $H2O3S$ | 82.08 | S, 39.07 | MacPhee, 2019; |
| Urea | $CH_4N_2O$ | 60.06 | N, 46.64 | Mylavarapu et al., 2016; |
| Urea Phosphate | $CH_7N_2O_5P$ | 158.05 | N, 17.72 P, 19.60 | Mikkelsen and Jarrell, 1987; |
| Urea Sulfate | $CH_6N_2O_5S$ | 158.14 | N, 17.71 S, 20.28 | Mikkelsen and Jarrell, 1987; Whitlark, 2010; |

Oxidation of elemental sulfur ($S^0$) to sulfate ($SO_4^{2-}$) also releases $H^+$ (Eq. 16). Applying $NH_4^+$ and

$$2S^0 + 3O_2 \rightarrow 2H_2SO_4 \rightarrow HSO_4^- + H^+ \rightarrow SO_4^{2-} + H^+ \qquad \text{Eq. 16}$$
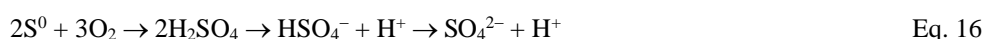
$S^0$ is common practice in turfgrass management and other areas of agriculture, but both reactions consume oxygen ($O_2$) in the process. Oxidation scavenges soil O that lowers soil redox potential as $pe$ + pH, which can foster anaerobiosis and development of black layer (Berndt and Vargas, 1992). Physically, black layer is a metal sulfide, which is a precursor to pyrite ($FeS_2$). When soil rich in $FeS_2$ (i.e., waterlogged soil) is drained, such as during golf course development, the oxidation of $FeS_2$ can result in soil pH values 1.5 to 3.5 creating acid-sulfate soils (Carrow et al., 2001) according to Eq. 17.

$$3FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3^- + 8H_2SO_4 \qquad \text{Eq. 17}$$

## Effects of Lewis-acids on Plants, Soils, and Microbes

Solubilization of soil components induced under low pH may lead to presence of toxic cations in soil solutions including the Lewis-acids $H^+$, $Al^{3+}$, and manganese ($Mn^{2+}$), which can impact roots and shoots. Deleterious effects of $Al^{3+}$ on roots are varied (Aggarwal et al., 2015). Aluminum becomes soluble at pH < 4.8 where it becomes available for root uptake as $Al^{3+}$ (Carrow et al., 2001; McCarty et al., 2003). Exposure to $Al^{3+}$ at sufficient concentration interferes with different plant functions (Baldwin et al., 2005; Panhwar et al., 2015; Tisdale et al., 1985). Functions include cell division, cell elongation, and enzyme processes in roots. Exposure to $Al^{3+}$ also decreases root respiration and interferes with uptake and transport of $Ca^{2+}$, $Mg^{2+}$, and $H_2O$. Aluminum alters root cell morphology causing thick, stunted, and brittle roots, poor root hair development, and swollen and damaged root apices (Aggarwal et al., 2015). Cell walls may be the site of maximum $Al^{3+}$ accumulation, where it leads to irreversible displacement of $Ca^{2+}$ in cell wall structure that is fundamental to cell wall stability (Aggarwal et al., 2015). Aggarwal et al. (2015) also reported $Al^{3+}$ decreased plasma membrane fluidity due to a 560-fold higher affinity for the phosphatidyl-choline surface than $Ca^{2+}$ ions. Root absorbed $Al^{3+}$ leads to production of reactive O species (ROS), including superoxide anion ($O_2^-$), which damages biomolecules like lipids and nucleic acids (Chauhan et al., 2021; Ranjan et al., 2021). Aluminum alters cell membrane potential and affects the activities of solute transporters in root tissues (Kar et al.,

2021). Permanent alteration of plasma membrane surface potential inhibits $H^+$-ATPase activity (i.e., a $H^+$ pump) that creates the electrochemical gradient needed for secondary transport (Ahn et al., 2001). It has also been reported that $Al^{3+}$ disrupts free cytostolic $Ca^{2+}$, causes callose deposition at the plasmodesmata, and inhibits mitochondrial respiration (Rahman et al., 2018). These effects can be induced within minutes at micro-molar concentrations of $Al^{3+}$ (Rahman et al., 2018).

Manganese toxicity can also be a limiting factor for growth of plants in acid soils, second only to $Al^{3+}$ (Zhao et al., 2017). Excessive $Mn^{2+}$ can trigger oxidative stress, inhibit enzyme activity, impede chlorophyll biosynthesis, and prevent uptake and translocation of $Fe^{2+}$ and $Mg^{2+}$ (Li et al., 2019; Liu et al., 2019; Santos et al., 2017). As with $Al^{3+}$ excess $Mn^{2+}$ induces oxidative damage due to rapid accumulation of ROS, causing chlorosis and necrosis in leaves (Zhao et al., 2017).

Overproduction of ROS including hydrogen peroxide ($H_2O_2$), hydroxyl radical ($OH^-$), and singlet oxygen ($^1O_2$) in response to $Mn^{2+}$ exposure causes lipid peroxidation and reduces net photosynthetic rate and the maximum and effective quantum yield of photosystem II (Liu et al., 2019). It may be possible that the chloroplast is a target, where $Mn^{2+}$ is reported to disrupt the thylakoid structure and photosynthetic $e^-$ transport (Zhao et al., 2017), although there appears to be limited information on this topic (Santos et al., 2017). Exposing Arabidopsis root tips to $Mn^{2+}$ reduced indoleacetic acid (IAA) biosynthesis and down-regulated expression of auxin carriers PIN4 and PIN7 (Zhao et al., 2017). Iron can also become toxic in acid soils interfering with enzyme activities and causing damage to membranes and chloroplast ultrastructure (Zahra et al., 2021). At pH < 4.5 direct injury from $H^+$ may occur damaging root membranes and growth of beneficial bacteria (Tisdale et al., 1985).

The character of CEC may be altered in acid soils affecting plant nutrition. Aluminum begins to saturate the effective cation exchange capacity (ECEC) at pH < 5.5; at pH 4 ≈ 100% of sites may be saturated with $Al^{3+}$ (Foth and Ellis, 1979). As a result, there is reduced availability of nutrient cations $Ca^{2+}$, $Mg^{2+}$, $K^+$, and $NH_4^+$; exchangeable acidic cations (i.e., $H^+$ and $Al^{3+}$) dominate ECEC but lack nutritional value and are toxic. Protonation of amphoteric hydroxyl groups on Fe and Al oxides in acid soils impacts variable charge, creating positive (+) charge sites reducing ECEC (Eq. 18). The CEC for thatch and humus may be 90-100% pH dependent (Carrow et al., 2001); amphoteric carboxylic and phenolic functional groups are protonated at low pH reducing ECEC (Tisdale et al., 1985).

$$Fe(OH)_3 + H^+ \rightarrow FeOH_2^+ \qquad\qquad Eq. 18$$

Acidic constituents are known to fix nutrients like P in acid soils directly limiting availability. At pH < 4.5 Fe begins to fix P with maximum fixation occurring between pH 4 to 3 (Barrow, 2017; Penn and Camberto, 2019). Between pH 4.5 and 6.5 fixation with $Al^{3+}$ occurs with a maximum at about pH 5.5. Precipitation of P with $Al^{3+}$ can be described as Eq. 19. Effectively,

$$Al^{3+} + H_2PO_4^- + 2\,H_2O \leftrightarrow AlPO_4 \bullet 2\,H_2O \text{ (variscite)} + 2\,H^+ \qquad\qquad Eq. 19$$
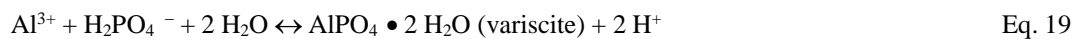
low pH promotes dissolution of Al and Fe oxides and hydroxides through hydrolysis (Lindsay, 1979, Sposito, 2008) resulting in solution $Al^{3+}$ and $Fe^{3+}$ that precipitate with P (Penn and Camberto, 2019). Low solution concentrations of P tend to interact with soil via ligand and anion exchange sorption, but high concentrations associated with P fertilization may precipitate with Fe and Al (Penn and Camberto, 2019).

Aluminum toxicity can also influence microbial community structure (Sullivan et al., 2017) by impacting specific groups of soil organisms (Lemire et al., 2010). Exposing *Pseudomonas flourescens* to $Al^{3+}$ disrupts aerobic formation of ATP by disrupting Fe proteins involved in the Kreb's cycle (Lemire et al., 2010); $Al^{3+}$ is a known inhibitor of the Kreb's cycle triggering accumulation of succinate (Gasmi et al., 2021). Aluminum toxicity in cyanobacterium (*Nostoc linckia*) increased as pH decreased from 7.5 to 4.5; $e^-$ transport was completely stopped at pH 6 and pH 4.5 when coupled with $Al^{3+}$ at 0.8 and 0.6 mM, respectively (Husaini and Rai, 1992; Pina and Cervantes, 1996). This research suggested aluminum binds with ATP at acidic pH making it metabolically unavailable. Manganese impacts growth of the pathogen *Phytophthora nicotianae* due to inhibition of sporangia production resulting from reduction of expression of genes csn4 and csn7 and by affecting antioxidant enzyme activity in sporangium (Lou et al., 2020). This effect is part of the reason $Mn^{2+}$ fungicides (i.e., Maneb) are effective in controlling certain pathogens.

## Conclusions

The non-metal cation $H^+$ is the principal of acidity; an $e^-$ deficient composite nuclear particle comprised of quarks held together by gluons vis strong force interactions. Being $e^-$ deficient with small size and large charge density $H^+$ behaves as a Lewis-acid. The metal cations $Al^{3+}$, $Mn^{2+}$, $Fe^{2+}$, and $Fe^{3+}$, along with molecular $CO_2$, which are common constituents in plant-soil systems, are also Lewis-acids. By their physical nature Lewis-acids accept $e^-$ pairs from ligands or Lewis-bases such as $OH^-$, $H_2O$, and $NH_3$ (Fig. 9) to produce Lewis acid-base adducts including $H_3O^+$, $H_2CO_3$,
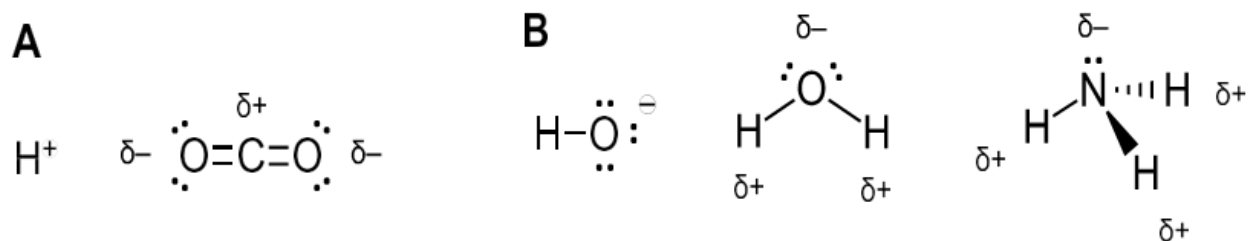
**Figure 9.** Lewis dot structures of electrophiles (A) and nucleophiles (B). A: $H^+$ and $CO_2$ are electrophilic Lewis-acids that form dative or coordinate covalent bonds with nucleophiles by accepting electron ($e^-$) pairs. B: nucleophiles (ligands) in plant-soil systems include $OH^-$, $H_2O$, and $NH_3$ have available $e^-$ pairs to share. Dots are unsatisfied $e^-$ pairs. Partial charges are shown.

$Al(H_2O)_6^{3+}$, and $NH_4^+$, which are sources of acidity to soils. Lewis acid-base chemistry explains formation of $H_2CO_3$ (Fig. 10) and the solvation of $Al^{3+}$ (Fig. 11).
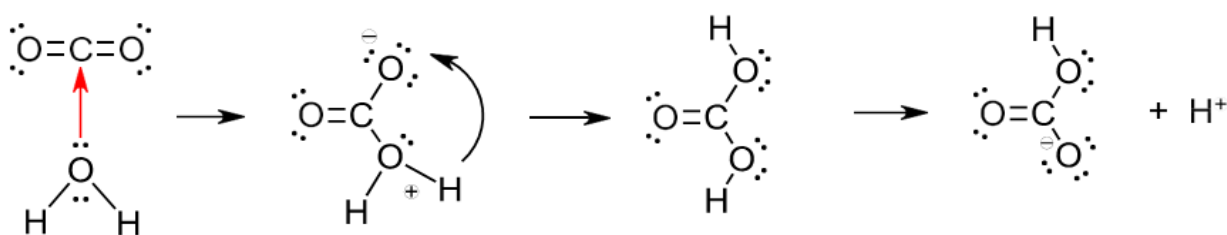


**Figure 10.** Attraction of an unsatisfied $e^-$ pair from the O in $H_2O$ to the partial charge on the C atom in $CO_2$ (red arrow) is a Lewis acid-base reaction with movement of the $e^-$ pair towards the C. The result is formation of the Lewis acid-base adduct $H_2CO_3$ and eventually $HCO_3^-$. While $CO_2$ is considered non-polar, having a net dipole moment of zero, each double bond is polar-covalent imparting a partial charge of $-0.29e$ on each O atom and a partial charge of $+0.58e$ on the C.
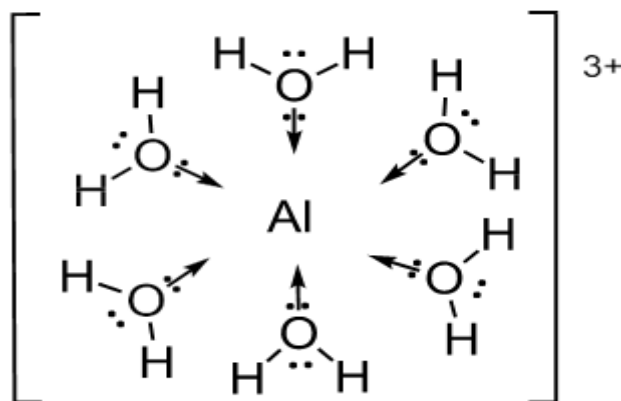


**Figure 11.** Formation of aluminum hexahydrate solvation complex ($Al(H_2O)_6^{3+}$) is a Lewis acid base reaction. The resulting cation is a coordination complex, with a coordination number = 6 and octahedral geometry; six lone pairs of $e^-$ surround the metal center forming dative bonds with it. Elemental Al has the $e^-$ configuration (Ne) $3s^2 3p^1$. When Al is oxidized and loses 3 $e^-$ the 3s, 3p, and two of the 3d $e^-$ orbitals hybridize into six new orbitals with equivalent energy levels resulting in a coordination number of six, using six orbitals to accept six lone $e^-$ pairs from $H_2O$. Due to affinity of Al for $e^-$, the $e^-$ pairs physically move towards the metal ion and the charge is spread over the entire cation not just the metal center

Solvated $Al^{3+}$ induces plant stress through oxidative effects on roots and physical impacts on ECEC leading to nutrient deficiencies. Solvation complexes such as $Fe(H_2O)^{3+}$ and complexes involving other metallic cations, referred to as aqua-ions and having the general formula $Me(H_2O)_n$, with varying coordination numbers, behave as Lewis-acids and may exhibit similar effects on plants and soils.

Due to affinity for $e^-$ pairs Lewis-acids are polarizing; ligands like $F^-$ and $OH^-$ having available $e^-$ pairs are polarizable. Lewis-acids effect distortion of anion $e^-$ distributions changing chemical-physical properties of substances. At low pH, the polarizing nature of $H^+$ causes distortion of $e^-$ orbitals of $OH^-$, weakening bonds of hydroxy-Al minerals leading to mineral dissolution and subsequent release of the solvation complex $Al(H_2O)_6^{3+}$. The polarizing nature of complexed $Al^{3+}$ results in hydrolysis and successive release of $H^+$ of coordinated $H_2O$ molecules (Eq. 7-10) hence input of additional acidity.

Describing the chemical-physical nature and Lewis-acid behavior of $H^+$ and other cations and molecules commonly found in plant-soil systems has broadened perspective of soil acidity and expanded the scope of thinking about soil reaction for turfgrass science and other plant science communities. Shaping the evolution of thinking about intrinsic soil characteristics like pH is a fundamental point of plant and soil sciences enabling advancement in research and management practices. The premise for agricultural research is to foster progression of agricultural management strategies and tactics. Having a more complete understanding of the nature and behavior of $H^+$ may be helpful in realizing this goal.

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