

ACIDITY AND ALKALINITY OF SOILS

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Summary

Soils that are significantly acidic or alkaline through all or part of the profile cover much of the Earth's land surface. The properties of soils that relate to their acidity and alkalinity, indicated by pH measurement, are fundamental to understanding the nature and behavior of many soils. Processes of acidification and alkalinization are important in the management and productivity of agriculture and in environmental management.

The pH of a soil sample reflects the dissociation of weak and strong acids and bases that are associated with the solutions, salts and mineral and organic compounds that make up soil materials. Change in pH mostly results from nitrogen, carbon and sulfur cycle effects that result from natural biological processes in soils, and rates of change may be accelerated by human activities through agriculture and industry. Examples of human activities that can accelerate or alter acidification or alkalization processes include fertilizer and lime application, product removal, irrigation and changes to water tables, changes to evapotranspiration conditions, or acid rain.

Soil pH varies in the landscape at different scales, from microsite to profile, toposequence, catchment and region. This continuum means that effective management of soil acidity and alkalinity should be considered both at the field scale, for crop production for example, and at the broader, catchment scale to control water quality and land degradation.

1. Introduction

Acidity and alkalinity of soils, as indicated by the measurement of soil pH, are important chemical properties that have a role in many of the ways that soils behave (see *Soil Chemistry*). pH is probably the most common analytical measurement made on soils. The availability of many plant nutrients and the capacity of soil materials to absorb and hold materials are often mediated by a soil's pH. It is usually the extremes of acidity or alkalinity that cause environmental problems, difficulties with growing plants, or with managing physical problems. In turn, a soil's pH reflects its chemical and mineralogical components and their relationships to the solutions that reside in soil pores. The composition of soils also controls their capacity to resist changes in soil pH – environmental perturbations often caused by human actions such as acid rain (see *Acid Deposition*), irrigation (see *Wastewater Treatment and Reuse for Irrigation*), agriculture (see *Organic Pollution from Agrochemicals*) and waste disposal (see *Chemistry of Hazardous and Solid Wastes and Leachates*).

2. World Distribution of Acidic and Alkaline Soils

Soils that are significantly acidic or alkaline cover much of the world's land area. Generally there are geographic, geological, biological and climatological reasons why soils tend to be either acidic or alkaline, and their natural state can be greatly modified by human actions. Soils profiles vary in their properties and may be either acidic or alkaline throughout, or may be either acidic or alkaline within different layers, though very generally the near surface layers tend to be more acidic than sub-surface layers. Producing a map of the world's acidic or alkaline soils is difficult for these reasons, and for reasons of spatial variability.

In areas where rainfall is low, soil leaching is usually insufficient to completely remove salts from soil profiles and it is common in these regions for soils to contain carbonate or bicarbonate ions that are concentrated by evapotranspiration processes. With increasing aridity, these alkaline materials and associated salts of sodium and gypsum

accumulate closer to the soil surface. Large areas in the semi-arid and arid climatic zones have accumulated calcium carbonates as rubble layers or hardened sheets that may act as a chemical or physical barrier to penetration by plant roots. The world's arid regions amount to about 50 million square kilometers, or about 30 percent of its land area, and their soils are usually alkaline, though some will be acidic as a result of past climates that were more humid. There are additional areas that have soils that are alkaline, such as the regions where loessial materials (wind-blown soil dust sourced from more arid regions) containing calcium carbonate have been deposited, or where soils have developed on calcareous parent materials. The latter are usually emerged calcareous marine or lacustrine sediments, but they may also contain significant sodium bicarbonate and carbonate in regions of low rainfall. At a more local scale, alkaline soils frequently develop in valley floors where carbonates and other salts accumulate due to the concentration of alkaline through flow or ground waters.

Soils that have acidified significantly, with pH values less than 5 or 5.5, tend to form in two climatic zones. The most important of these is perhaps the tropical belt of high annual rainfall where intense weathering of soil minerals and other processes have left acidified soils. This region is important because of its increasing population density and requirement for food production. There is also a large region at higher latitudes, principally in the northern hemisphere, where soils are acidic because of high effective rainfall and the accumulation of acidic organic matter. It is estimated that acidic soils cover about 30 per cent of the global land surface.

The remaining soils on the earth's land mass are regarded as predominantly neutral with respect soil pH, that is, their pH values are mostly between about 6 and 8. It is possible that these soils are in an environmental equilibrium where acidification processes and alkaline inputs are about equal, but it is likely that they are subject to net acidification if used for agriculture.

3. Soil pH and pH Buffering Capacity

3.1. Soil pH and the composition of the soil solution

The acidity or alkalinity of soil solution is measured using the pH scale. The ion activity product of water (pK_w) at 25° C is 14.0 and at a pH of 7 (neutrality), the activities of H^+ and OH^- are both 10^{-7} moles per liter ($mol L^{-1}$). The pH (Eq. (1)) of a soil solution in equilibrium with soil materials is the negative logarithm of the hydrogen ion activity:

$$pH = -\log_{10} (H^+) \quad (1)$$

(H^+) , the hydrogen ion activity, equals $\gamma[H^+]$ where γ is the activity coefficient and $[H^+]$ is the concentration of protons in the soil solution in moles per liter. Because the scale is logarithmic, a pH decrease of one pH unit indicates a ten-fold increase in hydrogen ion activity and a pH increase of one unit indicates a ten-fold increase on hydroxyl ion activity.

Most soil pH values are in a range between about 5 (10^{-5} mol L⁻¹ hydrogen ion activity) and 8.5 (3×10^{-9} mol L⁻¹ hydrogen ion activity). Acid sulfate soil conditions may result in soil pH values as low as about 2 and alkaline sodic soils may have pH values above 10.

Understanding soil acidity and alkalinity requires an understanding of the associated chemistry. Acidic and basic compounds in soils are defined by Brønsted and Lowry as being proton donors and acceptors, respectively. Strong acids and bases dissociate completely in solution (water in the case of soils). Most soil acids and bases are weak and are commonly dissociated about 1 percent.

Table 1 lists dissociation constants (pK_a) for some of the acids found in soil systems. When pH equals pK_a , the activities of an acid and its conjugate base are equal, that is, the acid is half dissociated. The dissociation of these acids and bases only buffers the pH of the soil solution significantly over a range of about 1 pH unit on either side of its pK_a . Because most soils are a mixture of mineral and organic components that are acids and bases, titrations of soil materials with acid or alkali produce buffer curves that reflect the net contribution from these components and may not appear similar to the buffer curves expected from, for example, simple polyprotic acids. In surface layers of soils where organic matter is usually accumulated, weakly dissociated organic acids buffer soil pH. Where soil pH is above about pH 6.5, the concentrations of bicarbonate and carbonate anions increase and it is the presence of salts and minerals of these anions, particularly sodium bicarbonate, that results in the very high pH values of alkaline sodic soils. Acid sulfate soils result from the oxidation of sulfides to form sulfuric acid and, if the acid neutralizing capacity of the soil material is low, pH values below 3 can result.

Formula of Acid	pK_a
H ₂ CO ₃	6.3
HCO ₃ ⁻	10.3
NH ₄ ⁺	9.2
HSO ₄ ⁻	2.0
H ₂ S	7.0
HS ⁻	12.9
H ₃ BO ₃	9.2
H ₂ SiO ₃	9.7
HCOOH (Formic)	3.8
CH ₃ COOH (Acetic)	4.8

Table 1: Dissociation constants (pK_a) for acids found in soil solutions

The ions present in soil solutions differ in amount and form depending on whether the soil pH is acidic or alkaline, reflecting the charge properties, equilibrium state, and mineral and organic materials that make up the soil. Most soil systems are not closed,

that is, they are subject to solutions and gases entering and leaving the profile and are therefore also in states of changing chemical equilibria. The specific form of ions present in solution are critical, especially as alkalinity or acidity increases, as species that are toxic to many biological processes, soil organisms and plants increase in concentration (see *Trace Elements, Speciation of Heavy Metals and Radioisotopes*).

The ions and complexes commonly found in soil solutions include:

- alkaline soil solutions, pH about 8

Cations: Ca^{2+} , Na^+ , Mg^{2+} , K^+

Anions: Cl^- , SO_4^{2-} , HCO_3^- , NO_3^- , HPO_4^{2-} , H_3BO_3 , organic ligands

- acidic soil, pH about 4

Cations: K^+ , Ca^{2+} , $\text{Al}(\text{organic ligands})^{2+}$, Mg^{2+} , Na^+ , Mn^{2+} and Fe^{2+}

Anions: SO_4^{2-} , Cl^- , H_2CO_3 , organic ligands, F^-

In alkaline soils, the ionic forms Na^+ , K^+ , Cl^- and NO_3^- predominate with increasing presence of bicarbonate and other complex forms of sulfate and bicarbonate. The increasing presence of bicarbonate and borate, and possibly the aluminate ion, often due to evaporative concentration and limited leaching, can result in very high soil pH and plant toxicities. Trace metal elements are present in such low concentrations that Fe, Mn and Zn become deficient.

In acidic soils, the ionic forms K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Mn^{2+} , Fe^{2+} , SO_4^{2-} and Cl^- predominate, with complex forms of aluminum (Al) with organic ligands, F and OH. As pH decreases, increasingly is the very toxic Al^{3+} released. The main ionic forms listed occur at close to 100 percent of the element present in solution and are therefore readily available to plants and, significantly, may also be readily leached. Plant nutrient deficiency for elements such as K, Ca and Mg can be common at low soil pH, usually because leaching loss has impoverished the soil.

3.2. Neutralizing Capacities, pH Buffer Capacity and Lime Requirement

The ability of soil materials to absorb the effects of acidic additions is often termed its acid neutralizing capacity (ANC; or, inversely, its 'alkali' or 'base' neutralizing capacity), that is, the ability of soil components to accept protons or hydroxyls. Although there may be some neutralizing capacity in the soil solution, it is the greater mass of solid, mineral material that contributes most to this capacity, especially below pH 5 and above pH 8. For example, acid neutralizing capacity may be provided by the dissolution of carbonate minerals in alkaline soils, the base saturation of the soil's exchange complex, or the decomposition of less weatherable aluminosilicate minerals in acidified soils. The adsorption reactions that involve the soil solution and ion exchange have fast reaction rates compared to dissolution reactions, but their capacity to act as proton sinks may be orders of magnitude less. The processes that result in soil alkalization or acidification can be defined as those that produce an increase or decrease, respectively, in ANC. ANC varies with soil pH but can be measured in a

general way for the solid components using Equation 2, where the brackets indicate molar quantities:

$$\text{ANC (solid)} = 2(\text{CaO}) + 2(\text{MgO}) + 2(\text{K}_2\text{O}) + 2(\text{Na}_2\text{O}) + 2(\text{FeO}) + (\text{NH}_3) - 2(\text{SO}_2) - 2(\text{P}_2\text{O}_5) - (\text{HCl}) - 2(\text{N}_2\text{O}_5) \quad (2)$$

The ANC of the soil solution generally simplifies to equation 3, where A indicates organic anions:

$$\text{ANC (solution)} = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + (\text{OH}^-) + (\text{A}^-) - (\text{H}^+) \quad (3)$$

The capacity of soils to resist pH change when challenged by acid or alkaline inputs is termed its pH buffer capacity. It is usually expressed as the amount of protons (H^+ , acidic) or hydroxyl (OH^- , alkaline) ions needed to change a specific mass of soil by one pH unit. More specifically, in agriculture, the alkali, usually calcium or magnesium carbonates, needed to increase the pH of an acidic soil to a desired pH by liming is termed its “lime requirement”. Fifty kilograms of calcium carbonate (CaCO_3) is equivalent to, and able to neutralize, 1 kmol of H^+ . In soil systems where changes occur, annual acidification rates are often expressed as the equivalent kmol $\text{H}^+ \text{ ha}^{-1} \text{ y}^{-1}$ or sometimes in kilograms of $\text{CaCO}_3 \text{ ha}^{-1} \text{ y}^{-1}$.

The pH buffering capacity of a soil is provided by its mixture of mineral and organic constituents and is modified by their surface properties, the electrical charge on which also changes with soil pH. Alkaline soils (pH > 7) that contain carbonate minerals may have considerable capacity to neutralize the effects of acidic inputs. For soils with pH in the neutral to moderately acidic range (pH 5 to 7), it is usually ion exchange reactions associated with clays and organic matter that control pH. Within this approximate range, the pH buffer curve of most soils is usually close to linear. Below pH values of about 5, stronger pH buffering in many soils is due to decomposition of clays and other remaining aluminosilicates, if they are present. The release of toxic aluminum, manganese and other ions at soil pH values less than 5 has detrimental consequences for the growth of many non-adapted plants and accelerated release of nutrient elements such as calcium, magnesium and potassium results in increased leaching loss and potential nutrient deficiency.

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Biographical Sketch

Richard Merry is an honorary research fellow at CSIRO Land and Water, Adelaide, South Australia. He is a graduate of the Universities of Tasmania and Adelaide. Over several decades his research has been strongly field-based in the disciplines of pedology, soil chemistry and agronomy. Specialist research topics include: soil acidification in crop and pasture soils, and in landscapes; acid sulfate soils in coastal and inland environments and wetlands; toxic metals distributions (derived from smelters, horticulture and urban sources) in soils and landscapes; soil analysis using mid infrared spectroscopy; sodicity and salinity; soil fertility.