Soil Acidification and its Impact on Plants

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Abstract

Acidic soils are widespread covering nearly 40% of the world's total arable land area. However, soils of certain regions are naturally acidic but an increase in soil acidification as a result of accelerating anthropogenic activities is becoming a global issue. High emissions of acid precursors (nitrogen, sulfur, and carbon dioxide) in the atmosphere are chiefly responsible for acid precipitation, which in turn is a pre-eminent factor for soil acidification. Long-term application of nitrogen fertilizers is a major contributor in acidification of agricultural soil. Soil acidification is an important edaphic stress, which leads to cation leaching, instability in the soil aggregate structure, increases metal toxicity, lowers the soil nutrient availability, and consequently affects the soil biological properties and plant performances. The present chapter aimed to assess the consequent effects of soil acidification on plants and the plant community structure. It includes causes, processes, plants' responses, and remedial measures to combat soil acidification due to increasing pollution. Different plants may show different sensitivity to acidity and have diverse an optimal pH range for nutrient uptake. Besides, depletion of basic cations (Na, Ca, Mg, and K) due to leaching and increased solubility of toxic metals (Al and Mn) in soil restrict the plant's access to water and nutrients, thereby causing severe injury to roots, a reduction in crop yield, and an increase in plant susceptibility to pathogens. Plant diversity, species richness, and occurrence of species are significantly influenced by acidification of soil. Alteration in the plant community structure, in turn, may affect the ecosystem structure and functions. Acidification of soil could plausibly be ameliorated by nutrient management practices and by addition of acid-neutralizing substances.

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P. Singh et al. (eds.), *Plant Responses to Soil Pollution*,
https://doi.org/10.1007/978-981-15-4964-9_1

Keywords

Soil acidification · Plants · Crops · pH · Atmospheric depositions · Biodiversity

1.1 Introduction

The term "soil" has been derived from the Latin word "solum", which means part of the earth's crust that has been changed as a result of soil-forming processes. Soil (also known as the pedosphere) is the material, which slowly develops as a thin layer on the earth's surface over time. It is mainly composed of organic matter, weathered mineral particles, living organisms, liquids, and gases; hence is one of the most important earth's natural resources essential for living beings (Bhattacharyya and Pal 2015). Soil is a zone of plants' growth where plant nutrients are stored through the interaction of diverse factors such as water, air, sunlight, rocks, flora, and fauna**.**

Depending upon various biotic and abiotic factors in different regions across the globe, there are broadly 12 classes of soil, viz. alfisols, andisols, aridisols, entisols, gelisols, histosols, inceptisols, mollisols, oxisols, spodosols, ultisols, vertisols, and others (rocky lands, shifting sand, and ice/glacier) (Fig. 1.1, Table 1.1).

1.1.1 Properties and Functions of the Soil

General physicochemical properties of the soil include texture (percentage of silt, clay, and sand in soil), temperature, pH, salinity, bulk density, porosity, moisture

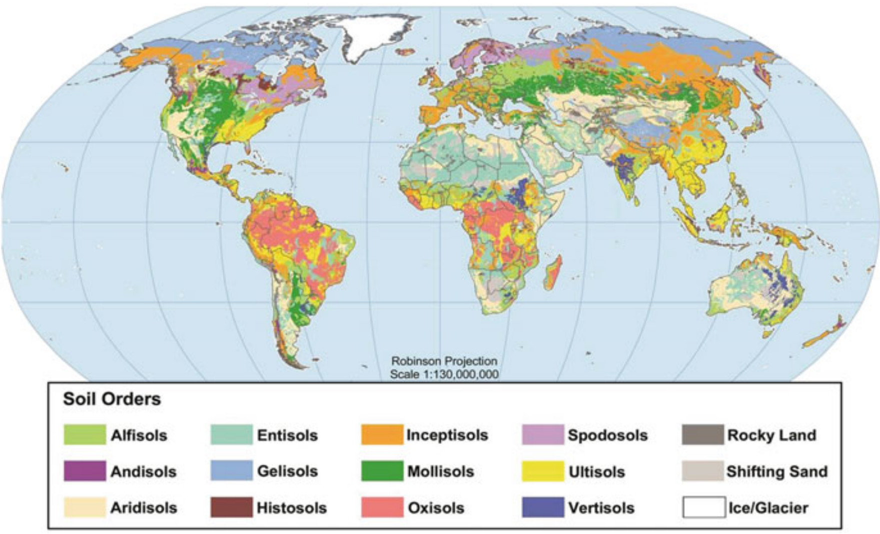

Fig. 1.1 Types of the soil in various regions of the world (Source: Soil Survey Division 2005)

Table 1.1 Key characteristics and occurrence of different classes of soil in various parts of the world

No.	Class	Key characteristics	Regions
1.	Alfisols	Commonly found in cool to hot humid areas, especially under forest and savannah grassland vegetation. Fertile with moderate to high base saturation Clay in subsoil horizons Covers about 10% of the world's ice-free land area	Europe, Russia, southern part of the USA, Mississippi, and Ohio river valleys in the USA
2.	Andisols	Form in volcanic ash and cinders Not extensively weathered High natural fertility and productivity High organic matter, low bulk density and can easily be tilled. Covers 1% of the world's ice-free land area	Limited geographic distribution
3.	Aridisols	Generally light in color and extensively found in tropical latitudes, rain shadow areas, and arid climates. Low organic matter with lime and salt accumulations Water deficient with low productivity High potential for land degradation due to overgrazing Occupies 12% of the world's ice-free land area	South-western and northern part of the USA, Australia, and many middle east regions
4.	Entisols	Little or no profile development in deep regolith Found at the site of unstable environments (floodplains, sand dunes, or those found on steep slopes) Vary in productivity potential	Geographically extensive and commonly found with aridisols
5.	Gelisols	Soil associated with permafrost and have limited profile development Soil organic matter on surface Productivity limited by short growing season Covers approximately 9% of the world's ice-free land area	Northern regions of Russia, Canada, and Alaska
6.	Histosols	Organic peat lands or boggy soils Consist of more than 20% organic materials by mass Found in cool and marshy areas Extent of the world's ice-free land area is 1%	Found mainly in geographically high latitude areas or other marshy wetlands

(continued)

Table 1.1 (continued)

No.	Class	Key characteristics	Regions
7.	Inceptisols	Found in the beginnings of soil profile development Variable productivity potential Covers 10% of the world's ice-free land area	Mainly in mountainous regions but occur almost everywhere
8.	Mollisols	Mineral soils developed under grassland vegetation Rich in organic matter Very fertile due to high clay and organic matter contents Extent of the world's ice-free land area is 7%	Eastern Europe, Russia, China, southern, and northern part of the USA
9.	Oxisols	In hot and humid climates with high annual rainfall Highly-weathered soils dominated by iron and aluminum oxides Low in fertility and high in soil acidity Physically stable soils with low shrink-swell properties Covers 8% of the world's ice-free land area	Equatorial latitudes
10.	Spodosols	Form in sandy materials under coniferous forest vegetation Associated with a wet and cool climate Coarse textured, high leaching potential, high organic matter, Fe and Al oxides contents. Acidic in nature and low soil fertility. Extent of the world's ice-free land area is 4%	Northern Europe, Russia, and north-eastern part of the USA
11.	Ultisols	Intensely weathered soils of humid areas Subsurface clay accumulations Low in fertility and high in soil acidity Covers 8% of the world's ice-free land area	Occur extensively in the south-eastern part of the USA, China, Indonesia, and equatorial regions of Africa
12.	Vertisols	High content of clay minerals, Dark colored with variable organic matter content (1–6%) Typically form in limestone/basalt/ topographic depressions Commonly formed in warm, subhumid, or semi-arid climates Extent of the world's ice-free land area is 2%	North-Eastern Africa, India, and Australia with smaller areas scattered worldwide.

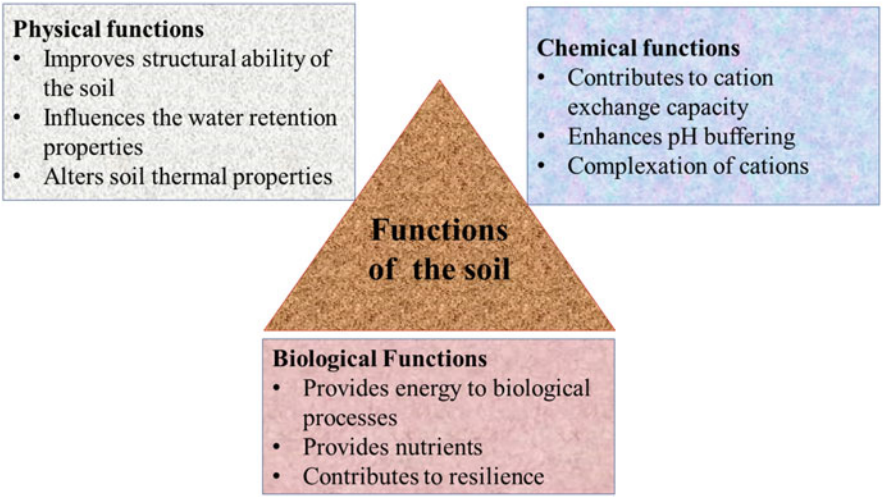

Fig. 1.2 Physicochemical and biological functions of the soil

content, particle size, water-holding capacity, exchangeable cations (Ca^{2+}, Na^+, Mg^{2+}, K^+, Al^{3+}, and Fe^{3+}), cation exchange capacity, sodium exchangeable percentage, total nitrogen (N), available nitrogen (nitrate-N and ammonia-N), available phosphorous, total phosphorous, total organic carbon, organic and inorganic carbon, total and bioavailable metal(oid) contents (aluminum, Al; iron, Fe; zinc, Zn; nickel, Ni; selenium, Se; boron, B; copper, Cu; cobalt, Co; magnesium, Mg; manganese, Mn; cadmium, Cd; chromium, Cr; arsenic, As; and lead, Pb), humic acid, organic, and inorganic pesticides (Pandey et al. 2014; Gautam et al. 2017; Albers et al. 2019). Besides, microbial biomass, total enzymatic activities, activities of enzymes (dehydrogenase, peroxidase, alkaline phosphatase, polyphenol oxidase, urease, catalase, and nitrogenase), root exudates, soil basal respiration, and metabolic quotient are certain widely used biological parameters to assess the health of the soil (Choudhary et al. 2013; Pandey et al. 2014; Gautam et al. 2018).

The soil functions within an ecosystem vary greatly from one place to another depending upon the parent material, position on the landscape, age of the soil, climatic variables, and animals' and plants' diversity (Fig. 1.2) (Schoonover and Crim 2015).

Soil functions are thus crucial for the biosphere and its main ecological roles include:

(a) **Support for structures**: The soils are widely used in making causeways and roads, as a foundation for buildings and bridges as well as for the establishment of agriculture crops and forestry.
(b) **Medium for plant growth**: The soil consists of four main components, viz. mineral matter (45%), organic matter (5%), water (25%), and air (25%) (Fig. 1.3). It is a source of physical support (root anchorage), air (ventilation),

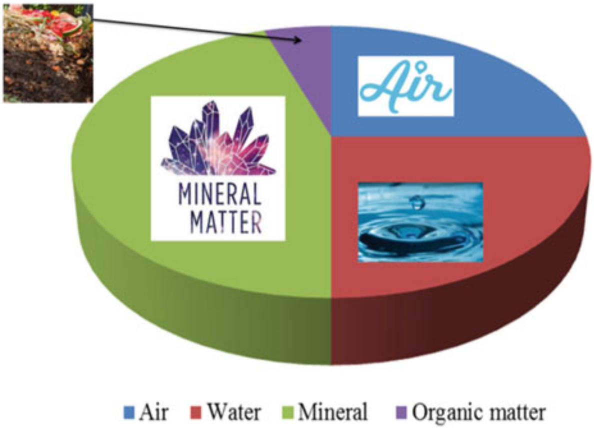

Fig. 1.3 Major components of the soil

water (holds rainwater, surface, and groundwater so that it can be utilized by plant roots), temperature moderation (acts as insulation for plants from extreme hot and cold conditions), protection from xenobiotics (removes toxic gases, decomposes, and absorbs organic/inorganic toxins), and supply nutrients (essential for their growth and development).

(c) **Regulate water supply**: The soil plays a pivotal role in cycling of freshwater. Water ending up into the water-body, i.e., lakes, rivers, estuaries, and aquifers, either traveled over the surface or through the soil. Soil filters and regulates water supply by restoration after precipitation. Management of the land area thus has a significant influence on the purity and amount of water that finds its way to aquatic systems.

(d) **Habitat for organisms**: Soil offers a shelter to billions of organisms (predators, prey, producers, consumers, and parasites). It provides a range of niche and habitat as well as types of habitats, which determine the specific organisms residing into it such as.

- Water-filled pores for swimming organisms like roundworms.
- Air-filled pores for insects and mites.
- Areas enriched in organic matter for various algae, fungi, parasites, lower, and higher plants.
- Areas with varied acidic, basic, and temperature regions for extreme dwellers.

(e) **Recycle wastes**: The soil system plays a significant role in nutrient cycling as soils have the ability to incorporate great quantities of organic waste, which then form humus. It converts the mineral nutrients of the wastes into utilizable constituents and has the ability to return carbon into the atmosphere in the form of CO_2. Plant residues and manures added to the soil increase nutrient concentrations, thereby enhancing the soil fertility.

1.1.2 Significance of pH

The pH is the measure of alkalinity and acidity of the soil (Fig. 1.4). Based on pH, the soil can be categorized into the following classes: extremely acid ($\leq$4.4), very strongly acid (4.5–5.0), strongly acid (5.1–5.5), moderately acid (5.6–6.0), slightly acid (6.1–6.5), neutral (6.6–7.3), slightly alkaline (7.4–7.8), moderately alkaline (7.9–8.4), alkaline (8.5–9.0), and strongly alkaline ($\geq$9.0). The pH scale (Fig. 1.4) shows various types of soils and their comparative relation with acidic and basic constituents based on their pH. Soil pH is one of the prime parameters that govern the soil aggregate stability, nutrient availability, metal toxicity, and biological activities (Goulding 2016).

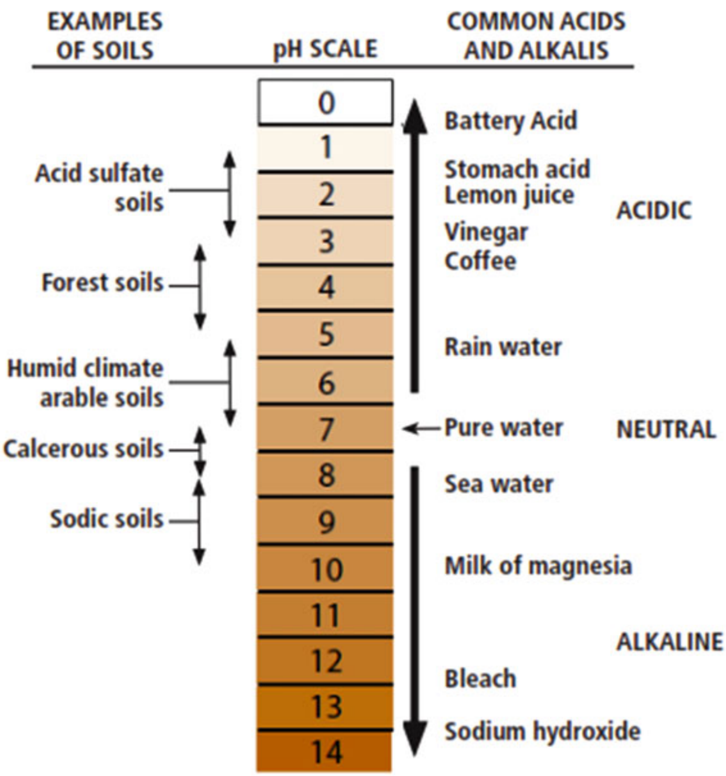

Fig. 1.4 The pH scale (Source: McCauley et al. 2009)

1.2 Soil Acidification

The soil acidification is a process where pH of the soil decreases over time. It is defined as a decrease in acid-neutralizing capacity (ANC) or an increase in base-neutralizing capacity (BNC) resulting in an increase in acid strength as represented by a decrease in soil pH (Blake 2005):

$$\text{Soil acidity } (+\Delta\text{BNC}) = \text{-(soil alkalinity)} = \Delta\text{ANC}$$

Pedogenic acidification processes in aerated soils are (1) an addition of strong acid (H_2SO_4 and HNO_3) into soil through acid deposition, (2) release of many organic acids and H^+ ions into the soil by plants and soil microbes and (3) uptake of basic cations by biota.

Soil acidification under natural conditions mainly occurs due to weathering of parent materials having high silica (rhyolite and granite), and sand with low buffering capacities and in regions with high precipitation (McCauley et al. 2009). Precipitation leads to leaching of base-forming cations with a simultaneous lowering of soil pH. Naturally occurring acidic soils are commonly found in areas at higher elevation, mining sites containing pyritic (Fe and elemental S) minerals, forest soils, and in areas where soils are formed from the acid-forming parent material. The process of soil acidification nowadays has been accelerated by human-induced activities such as agricultural practices, mining, metallurgical processes, etc. For instance, almost 5,00,000 ha of agricultural and rural land have acidified in Queensland (Rolfe et al. 2002). Intensive agricultural practices in coastal areas with a high precipitation rate are most at the risk of soil acidification (Duan et al. 2016). Soil acidification is a consequence of a dramatic increase in anthropogenic acid deposition originating chiefly from atmospheric sulfur dioxide (SO_2) and nitrogen oxides (NO_x) during agricultural fertilization and fossil fuel combustion (Zhao et al. 2009; Yang et al. 2012).

Soil acidification may have a negative impact on the entire ecosystem because soil is a fundamental interface where the atmosphere, lithosphere, hydrosphere, and biosphere meet. Any undesirable change in the baseline properties of soil affects a range of natural resource functions, which include soil micro-flora and fauna, vegetation structure, terrestrial animals, aquatic biota, atmospheric constituents, weed control, infrastructure, and human health (Singh and Agrawal 2004; Yang et al. 2015; Chen et al. 2016; Stevens et al. 2018). Some of these have wide community impacts through soil degradation and include the loss of native biodiversity that may impact on recreation and tourism (Singh and Agrawal 2007; Tian and Niu 2015).

1.2.1 Causes of Soil Acidification

Acidification of soil is accomplished through protons (H^+), which release into the soil mainly by atmospheric acidic substances, cation assimilation by plants, mineralization of anions of organic matter, weak acid deprotonation, mineral weathering, oxidation-reactions, etc. Sources of soil acidification are given in the following subsections.

1.2.1.1 Ammonium Fertilizers

Ammonium ions from the nitrogenous fertilizers form nitrate and hydrogen ions. Uptake of nitrate ions by the plants release hydroxide (OH^-) ions to maintain the ionic balance. Hydroxide ions combine with positively charged hydrogen ions to form water. On the other hand, when nitrate ions are not taken up by the plants, leaching of these ions occurs and hydrogen ions are left in the soil, thus causing acidification. Hydrogen ions are tightly bound to soil particles as compared to other ions, which causes leaching of other positive ions such as Na^+ and Ca^{2+}. (Blake 2005) thereby increasing the concentration of H^+ ions. Also, in the process of plant uptake of nitrate, one H^+ ion is left that cannot be neutralized by OH^- ions, cumulatively contributing to soil acidification (Bolan et al. 1991). Excessive application of fertilizers thus leads to soil acidification. Use of N-fertilizers lowers the ANC of soil (Van Breemen et al. 1984). Bolan et al. (2005) reported that ammonium sulfate has the highest acidity equivalence (i.e., the required number of parts by weight of lime to neutralize the 100 parts of fertilizer.) of 110, followed by ammonium chloride, urea, diammonium phosphate, ammonium nitrate, etc.

Tian and Niu (2015) reported a reduction in soil pH on N addition. The effect was different on different ecosystems such as grassland, tropical, and temperate forests, which showed a significant difference while boreal forest soil pH was not much affected by N addition. Tian and Niu (2015) also reported that NH_4^+ and NO_3^- forms of fertilizers are more contributing to soil acidification than the NH_4^+ form.

1.2.1.2 Atmospheric Depositions

Atmospheric depositions of N and S contribute to soil acidification (Singh and Agrawal 2007). Emissions of SO_2 and NO_x from combustion processes are chief sources of soil acidification in the region of temperate forest (Singh and Agrawal 2007). China has controlled its S emission since 2001, yet the Pearl river delta soil is acidified due to S deposition (Huang et al. 2019).

Acid rain has a remarkable contribution in acidification of soil (Singh and Agrawal 2007). SO_2 and NO_x are the gases responsible for acid rain. Acid rain has pH generally less than 5.6 and H^+ ions more than 2.5 μ eq. L^{-1} (Evans 1984). Various anthropogenic activities are responsible for emission of these gases such as fossil fuel combustion, industrial, mining processes, etc. Natural sources include volcanic eruption, oceans, lightening, and biological processes (Singh and Agrawal 2007). These gases react with water and other pollutants and cause acidification of rain. Wet depositions of acid directly add acid to the soil and when dry deposition occurs SO_2 mixes with soil water and produces acid (H_2SO_4). Similarly, NH_4^+ ions mix with water and produce nitric acid. Many reports showed that acid rain caused a significant decrease of soil pH (Singh and Agrawal 2007).

Increasing concentration of CO_2 in the atmosphere is also a source of soil acidification. Atmospheric CO_2 reacts with water to form carbonic acid whose deposition may lower soil pH. Oh and Richter Jr (2004) reported that the soil CO_2 concentration increases proportionally with the increase of atmospheric CO_2.

1.2.1.3 Leguminous Crops

Haynes (1983) reported that cropping of legumes either for short or long duration lowers the pH of soil. Legume cultivation induces soil acidification due to disturbance in the C and N cycles. Mineralization and nitrification processes cause NO_3^- leaching and legume plants during N_2 fixation uptake more cations than anions, thereby releasing more H^+ ions from roots to the soil environment. When legume biomass is removed from the soil, pH of soil is reduced more, causing acidity (Yan et al. 1996). Different leguminous species have different acidifying capabilities. Legumes growing in the tropical region are less effective in acidifying soil than in the temperate region (Tang et al. 2013). Acidification of subsurface soil is more common as legumes have a deep root system. Surface-acidified soil can be easily reclaimed through liming or other methods; thus, subsurface soil acidification by leguminous plants is of more concern (Tang et al. 2013). Dinkelaker et al. (1989) reported that legumes induce more acidification in soil deficient with phosphorous (P). In young plant residue, organic N is higher and organic anions are low, which reduce the pH of soil and older plant residue tends to increase the pH (Yan et al. 1996). Thus, residue return is an important agricultural practice to prevent soil acidification.

Leaching of carbonates leads to soil acidification as carbonates in soil act as buffer. Wang et al. (2015) reported that up to a certain level ($<1\%$), carbonate in soil is required to reduce the drop level of carbonates to maintain the soil pH and to reduce the toxic effects of heavy metals.

1.2.1.4 Organic Acids

Formic acid, acetic acid, and oxalic acid are the major organic acids that are present in acid rain (Sun et al. 2016). There are two sources (direct and indirect) of organic acids in the atmosphere, contributing significantly to acid rain formation (Singh and Agrawal 2007). The direct sources of organic acids are fossil fuel and biomass burning, emission from vegetation and automobiles, volcanic eruptions, lightening, etc., whereas the indirect or secondary sources include secondary reactions involving the precursors such as terpenes, isoprenes, aldehydes, marine olefins, hydrocarbons, etc., and sunlight that occur in the atmosphere.

1.2.1.5 Industries

Mining and industrial processes such as coal and sulfide-containing ores' mining, manufacturing of electronic stuffs, textiles, tanneries, and food-processing activities, and drain acids in the environment are also some important contributors of soil acidification (Bolan et al. 2005). Many other industries discharge their acidic effluents that cause acidification of soil. Industries also emit SO_x and NO_x in the atmosphere that are deposited on soil, either in wet and dry forms and reduce soil pH.

1.2.2 Process of Acidification

Hydrogen ions in soil come from a wide range of sources including natural biogeochemical cycles:

1.2.2.1 Carbon Cycle

Carbon dioxide from the atmosphere enters the soil and forms carbonic acid, which further dissociates and adds H^+ ions to the soil. Similarly, organic acids also produce H^+ ions. The substrates for the reactions are available through various natural and anthropogenic processes and the processes generally occur in the forward direction (Robson 2012).

$$\mathrm{CO_2 from\ atmosphere} \rightarrow \mathrm{CO_2 + H_2O} \leftrightarrow \mathrm{H_2CO_3} \leftrightarrow \mathrm{HCO_3^-}$$
$$\leftrightarrow \mathrm{CO_3^{-2}}\text{-Inorganic reaction}$$

$$C_6H_{12}O_6 \leftrightarrow RCOOH/ROH \leftrightarrow RCOO^-/RO^-\text{-Organic reaction}$$

1.2.2.2 Nitrogen Cycles

Several forms of N present in soil deposited through the atmosphere or through anthropogenic activities interchange forms and the dissociated H^+ ions are added to the H^+ ion pool of the soil. In the N cycle, plants share equal contribution in soil acidification, as the process of uptake and assimilation of NH_4^+ and NO_3^- as well as N fixation directly or indirectly releases H^+ ions in soil. Similarly, processes of ammonification, nitrification, and volatilization of NH_4^+ cause acidification of the soil (Bolan et al. 1991). Nitrification of organic N reduces pH of the soil (Yan et al. 1996).

Nitrogen from the atmosphere, fertilizers, and other organic sources →

$$RNH_2 \leftrightarrow NH_3 \leftrightarrow NH_4{}^+ \leftrightarrow NO_3{}^-$$

$$Volatilization\ of\ NH_4{}^+ \rightarrow NH_4{}^+ \leftrightarrow NH_3 + H^+$$

1.2.2.3 Miscellaneous Processes

Sulfur and P cycles also contribute to addition of H^+ ions in soil that leads to acidification (Robson 2012).

Weak hydroxide-forming cations such as Al, Mn, and Fe either in their exchangeable forms or bound onto clay particles and/or organic matter react with water and release H^+ ions in the soil (Blake 2005).

$$\mathrm{Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+}$$

$$Al^{3+} + 2\,H_2O \rightarrow Al(OH)_2{}^{+} + 2\,H^{+}$$

Organic matter in soil after decomposition also releases H^+ ions (Bolan et al. 1991). Likewise, mineralization of organically bound N followed by nitrification of the product release H^+ ions in soil.

$$CO_2 + R\text{-}CH_2OH \rightarrow RCOO^{-} + H_2O + H^{+}$$

$$R - C - NH_2 \rightarrow NH_3 + H^{+} \rightarrow NH_4{}^{+} + 2\,O_2 \rightarrow NO_3 + H_2O + 2\,H^{+}$$

1.2.2.4 Acid Rain

For the formation of acid rain, oxides of S and N play lead roles. These oxides react with water in the presence of sunlight and form acid mists. These mists after condensation precipitate in the form of acid rain. Reactions involved in the formation of acid rain are given below.

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow H^{+} + HSO_3{}^{-}$$

$$HSO_3 + O_3 \rightarrow SO_4{}^{2-} + H^{+} + O_2$$

$$2\,SO_2 + O_2 \rightarrow 2\,SO_3{}^{-}$$

$$SO_3{}^{-} + H_2O \rightarrow H_2SO_4$$

$$N_2 + O_2 \rightarrow 2\,NO$$

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

$$4NO_2 + O_2 + 2\,H_2O \rightarrow 4\,HNO_3$$

$$O_3 + NO_2 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3$$

Ozone (O_3) molecules are also responsible for the formation of acid rain through generation of hydroxyl radicals, which help in breakdown of S and N oxides and other organic molecules to form organic acids (formic and acetic acids) (Singh and Agrawal 2007). Formic acid is produced by oxidation of formaldehyde. Hydrated formaldehyde is produced when formaldehyde combines with water, which in turn reacts with hydroxyl radicals to form formic acid. Reactions for organic acid formation are:

$$HCHO + H_2O \rightarrow CH_2(OH)_2$$

$$CH_2(OH)_2 + OH \rightarrow CH(OH)_2$$

$$CH(OH)_2 + O_2 \rightarrow HO_2 + HCOOH$$

1.3 Effects of Acidification on Soil Properties

Soil acidification poses influential impacts on soil fertility, biological activity, and plant productivity (Table 1.2). Acidification of soils either due to natural or anthropogenic interventions may cause the following problems:

1.3.1 Water Availability

Soil acidification alters the structural stability of soil, which ultimately affects its porosity and water-holding capacity. This, in turn, may limit the plant's ability to use soil moisture.

1.3.2 Soil Aggregate Instability

An increase in the availability of clay minerals such as oxides and hydroxides of Al and Fe plausibly results in a poor soil structure and irreversible damage to the clay content of soil. A lack of Ca in soil also causes soil structural problems (Pal et al. 2016).

Table 1.2 Effects of pH on the availability of nutrients and metals in the soil

pH range	Effects
$<$6.0	Usually have a low availability of N, K, S, P, Ca, mg, and molybdenum (Mo), whereas solubility of heavy metals such as Al, Fe, Ni, co, cd, Cr, as, Pb, etc. is high under acidic conditions.
6.0–7.0	Favorable for plant growth because most plant nutrients are readily available in this pH range. However, some plants sustain at pH either above or below this range.
6.6–7.3	Favorable for microbial and enzymatic activities, thereby affecting availability of nutrients in soils.
$>$7.8	Potassium, S, Ca, Mg, and Mo are abundant, while there is inadequate availability of N, Fe, Mn, Cu, Zn, and other toxic metals
$>$8.5	Phosphorous and B are readily available

1.3.3 Nutrient Cycling

Soil's ability to hold nutrients is significantly related to its cation and anion exchange capacities, which in turn are influenced by pH (McCauley et al. 2017). Soils with higher amounts of clay and/or organic matter have higher cation exchange capacity and so are able to bind more cations when compared to silty or sandy soils (McCauley et al. 2017). Maximum plant nutrients are optimally available in the pH range of 6.5 to 7.5 (Dinesh et al. 2014). This pH range is also suitable for plant root growth. Availabilities of Cu, Fe, Zn, Mn, and Al are increased in acidic soils because at low pH, fewer metal ions are adhered to the soil surface, readily found in soil solution, and thus are more available for plant uptake. At low pH, S and base-forming cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) are displaced by H^+ ions and may not be bioavailable because of their loss from the soil through leaching or uptake (McCauley et al. 2017). Nitrate is equally available across soil pH levels because it doesn't bond much to the soil. In general, N, P, K, Ca, Mg, and S are more available within soil pH is 6.5 to 8, while B, Cu, Fe, Mn, Ni, and Zn are more available within soil pH is 5 to 7. The soil pH below 6.0 may cause deficiencies of N, P, S, K, Ca, and Mg in the soil due to their reduced bioavailability under acidic conditions (Fig. 1.5). Maximum numbers of plant nutrients (especially micronutrients) tend to be unavailable at pH above 7.5 except Mo, which is abundant at moderately alkaline pH (Fig. 1.5). Plants showed poor root growth performance under acid soil conditions due to less availability of plant nutrients, which are essential for growth (Matsumoto et al. 2017). However, N, S, and K are the main plant nutrients, which are less affected by soil acidification to some extent.

Phosphorus is directly affected by soil conditions and becomes unavailable to plants at high and low soil pH. At pH greater than 7.5, phosphate ions react with Mg and Ca to form insoluble complexes. Similarly in acidic soil, phosphate ions react with Al and Fe to form least soluble compounds (Penn and Camberato 2019).

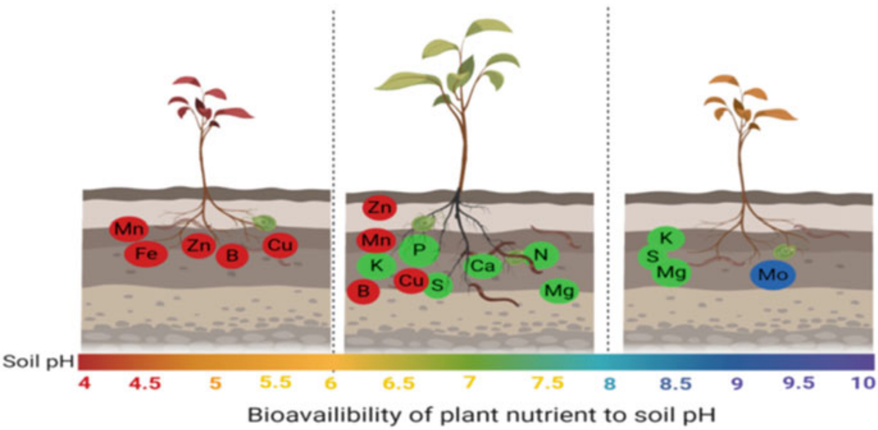

Fig. 1.5 Plant nutrient availability in acidic, neutral, and basic soil pH ranges

$$
\begin{array}{lll}
Ca^{2+}(H_2PO_4) + 2\ Ca^{2+} & \rightleftarrows & Ca_3(PO_4)_2 + 4H^+ \\
(\text{Soluble}) \quad (Adsorbed) & & (\text{Insoluble}) \\
Al^3 + (H_2PO_4)_2 & \rightleftarrows & 2H^+ + Al\,(\text{OH})_2 H_2PO_4 \\
(\text{Soluble})(\text{Insoluble}) & &
\end{array}
$$

1.3.4 Metal Toxicity

Mobility of metals increases with a decrease in soil pH, which when crosses certain threshold levels may cause toxic effects on living organisms (Gautam and Agrawal 2019). Contents of metals such as Cd, Cr, As, and Pb are deleterious for soil biota, growth, and development of plants (Chibuike and Obiora 2014). At pH less than 5.5, high concentrations of Al and Mn in the soil solution can reach toxic levels and limit crop production (McCauley et al. 2009). Aluminum is toxic to plants and severely restricts root growth. Acidity of soil may increase the net loss of soil nutrients such as Mn, Cu, Fe, B, and Zn (Ahmadpour 2011). Low levels of Ca and Mg due to competitive behavior with metals may cause stock health problems such as milk fever and grass tetany (Boom 2002).

1.3.5 Soil Biological Properties

Soil microorganisms, primarily bacteria and fungi, have the ability to solubilize the nutrients, cause decomposition of organic matter, and regenerate secondary mineral nutrients. Acidification of soil reduces and even stops the activity and survival of useful soil organisms such as nitrogen fixers, decomposers, and nutrient recyclers (Jacoby et al. 2017). Soil acidity is thus becoming a major problem in modern agricultural systems, which are affecting the soil microbial community (Li et al. 2017). Moreover, the above-mentioned processes occur at desirable pH ranges and acidification of soil lowers the process and impede with soil ecological balance (Hayakawa et al. 2014). Rousk et al. (2010) and Lauber et al. (2009) reported that microbial diversity is often highest in near-neutral soils and significantly lowers in acidic soils.

Microbial activity is considerably reduced at pH 5 and below (Rashid et al. 2016). Certain "specialized" microorganisms, such as nitrifying and nitrogen-fixing bacteria associated with many legumes, generally perform poor when soil pH falls below 6 (McCauley et al. 2009). Nodulation in leguminous plant roots is regulated by soil pH. In acidic soil, more than 90% of nodule formation fails to persist in legumes such as cowpea, alfa-alfa, pea, and soybean in both determinate and indeterminate nodule formation (Ferguson et al. 2013). Furthermore, low soil pH limits both rhizobia survival, and root growth, and hence reduces the chances of root's contact with enough bacteria, which help in nodule formation, resulting in nitrogen deficiency in soil (Ferguson et al. 2013). For instance, alfalfa (a leguminous plant) grows best in soils with pH levels greater than 6.2 when associated nitrogen-fixing bacteria also grow well (McCauley et al. 2009). Nutrient availability of plants gets reduced and causes poisoning mainly due to a decline in the rate of mineralization of nutrients by microorganisms under acidic soil (Zhalnina et al. 2015). In acidic soil, fungal dominance is greater than bacteria because of its growing ability over a broader range of soil pH (Herold et al. 2012). The fungi can best grow in the pH range of 4.5–7.5; however, high bacterial growth occurs within pH ranging from 5.5 to 7.0. Under acidic conditions, soil is majorly regulated by fungal dominance, whereas at high soil pH, bacterial denitrification occurs (Chen et al. 2015).

Organic mats often form on the soil surface as a result of reduced biological activity and organic matter is not being broken down. Helpful soil microorganisms may be prevented from recycling nutrients (e.g., nitrogen supply may be reduced). When soil pH is extremely acidic or basic, pH modifications may be needed to obtain optimal growing conditions for specific crops.

1.4 Effects of Soil Acidification on Plants

The s*oil*s are the prime receptor of *acid deposition* and function as sink. Soil acidification coupled with acid precipitation has been reported to have deleterious effects on plants (Bolan et al. 2005). The increasing rate of soil acidity is a worldwide problem and approximately 40% arable land is acidic (Ferguson et al. 2013).

Acid deposition has been very much discussed and now gained public attention since the 1970s in the European countries and the USA. It has now become an important problem in South Asia (Menz and Seip 2004). Acidic deposition can affect higher plants either through foliar surfaces or through roots. Under acidic deposition, a wide range of sensitivity has been shown by plants. Young rootlets, root hairs, leaves, and apical shoots are highly sensitive to acidic conditions (Lal 2016). Plant growth can be affected by both directly and indirectly due to acidic deposition. The direct effect of acid deposition includes foliar damage, which ultimately causes physiological and morphological alternations, necrotic spots, and discoloration (Singh and Agrawal 2007; Kohno 2017). Plant structures, specifically leaves, are highly sensitive to acidic deposition (Du et al. 2017). Some commonly observed changes in plants due to acidic deposition are loss of cuticular waxes due to alteration in its chemical composition (Elliott-Kingston et al. 2014), increase in membrane permeability (Jin et al. 2013), reduction in chlorophyll content (Du et al. 2017), altered dark respiration rate (Liang et al. 2013), and loss of cold tolerance habit (Menz and Seip 2004). Acidic soil can also prevent seed germination and the rate of seedling survival (Liu et al. 2011).

Indirect effects of acidic deposition encapsulate crown dieback, reduction of canopy cover, and increase in plants' mortality (Huang et al. 2015). Such deleterious effects of soil acidification caused by acid deposition ultimately lead to a decrease in plant growth and under extreme conditions dieback of entire forest occurs (Huang et al. 2015). Moreover, the pH 3.8 and 5.4 were found to be moderately inhibiting the germination rate of seeds of Norway spruce, Scots Pine, and Silver birch (Reid and Watmough 2014). It was also reported that 34% of trees population showed discoloration of needles as well as leave losses. Around half of Germany's woodland got infected by diseases by the end of 1984. After witnessing great losses in a forest ecosystem in Germany, United States, and Europe have started intensive research toward measuring the ecosystem losses due to acid precipitation, its precursors, and their possible effects on forests (United Nations/European Commission 2002).

1.4.1 Effects on Crop Plants

Sensitivity of plants to soil acidification may vary widely with different species of plants and according to their tolerance level to acidity. Therefore, plants have different optimal soil pH ranges (Matsumoto et al. 2017). The impact of soil acidity on plant growth is likely to be insidious and a major impact occurs in the root region. Table 1.3 enlists certain crop and forage species, which are sensitive toward acidification below a certain pH level. Critical soil pH differs with crop cultivar and soil texture; therefore, critical values mentioned in the literature vary. Certain horticultural crops, temperate legumes, and grasses are highly sensitive to acidic soil conditions (such as carrot, cabbage, tomato, alfalfa, white clover, macadamia nut, banana, avocado, litchi, perennial ryegrass, and red clover) (Goulding 2016; Tomic

Table 1.3 Sensitivity of common crops and forage species and soil pH values below which growth may be restricted (adapted from Goulding 2016)

Sr. No.	Critical soil pH	Crop & Forage
1.	6.0	Field bean (*Vicia faba*)
2.	6.2	Lucerne (*Medicago sativa*)
3.	5.9	Barley (*Hordeum vulgare*) Sugar beet (*Beta vulgaris*) Pea (*Pisum sativum*) Vetch (*Vicia sativa*) Red clover (*Trifolium spp.*)
4.	5.6	Oilseed rape (*Brassica napus*) White clover (*Trifolium spp.*)
5.	5.5	Maize (*Zea mays*) Wheat (*Triticum aestivum*)
6.	5.4	Kale (*Brassica oleracea var. acephala*) Swede (*Brassica napus var. napobrassica*) Linseed (*Linum usitatissimum*) Turnips (*Brassica rapa*)
7.	5.3	Oat (*Avena spp.*) Timothy (*Phleum pratense*) Cocksfoot (*Dactylis glomerata*)
8.	4.9	Potato (*Solanum tuberosum*) Rye (*Secale cereale*)
9.	4.7	Fescue (*Festuca spp.*)

et al. 2018). Furthermore, crops such as cowpea, oat, finger grass, sweet potato, kikuyu grass, catalina love grass, and sugarcane are highly tolerant (Haling et al. 2011). Nevertheless, severe soil acidity has been known to limit the growth of all plant species, including the highly tolerant ones (Goulding 2016).

The soil pH is the chief indicator of the soil situation, which affects the yield and quality of crops by increasing unavailability of essential elements (Morgenstern et al. 2010). Schroder et al. (2011) reported that wheat yield losses in Oklahoma between 1995 and 2002 were accorded with a higher change in soil pH during the same period of time. Under low soil pH conditions, the plant root system gets damaged, resulting in poor growth performance with no typical leaf symptoms as are often seen under N or K deficiencies.

Specific damaging effects on plants due to high dissolution of harmful elements in acidic soil include:

1. Poor and abnormal root development of plants due to the release of high amounts of Al^{3+} in acidic soil. Morphologically, roots become stubby, short, and thick. Fine roots are poorly developed. Thus, insufficient water and nutrient uptake are facilitated by poor and inefficient root system (Rout et al. 2001; Bojorquez-Quintal et al. 2017).
2. The soils that have been acidified due to rigorous agricultural practices are prone to Mn toxicity. The legume crops such as dry beans growing in the temperate region showed sensitivity toward soluble forms of Mn at higher concentrations in soil. Recently, it has been observed that Southern Africa is facing a widespread problem due to increasing manganese toxicity (Reichman 2002).

1.4.2 Effects on Plant Community Structure

Plant community structure supports the ecosystem structure and functions such as productivity, resilience, and stability (Dovciak and Halpern 2010; Cardinale et al. 2012). Atmospheric deposition due to various anthropogenic activities leads to a significant increase in soil acidity due to fossil fuel combustion, agricultural emissions, waste discharges, etc. (Gheorghe and Ion 2011). The pathway to soil acidification-induced changes in plant community structure and productivity is illustrated in Fig. 1.6. Several studies have evidenced the decline in the plant community structure and productivity of aboveground plant accredited to an increase in soil acidification (Blake et al. 1994; Stevens et al. 2010; Van den Berg et al. 2011). Chen et al. (2013) reported higher reductions in plant species richness and productivity of *Stipa grandis*, *Agropyron cristatum*, *Achnatherum sibiricum, Cleistogenes squarrosa*, *Carex korshinskyi*, *Chenopodium aristatum*, *Salsola collina,* and *Chenopodium glaucum* in the second sampling year than in the first sampling year under seven different levels of acid additions (0, 2.76, 5.52, 8.28, 11.04, 13.80, and 16.56 mol H^{+} m^{-2} in the form of sulfuric acid solution) in the semiarid Inner Mongolian grassland region.

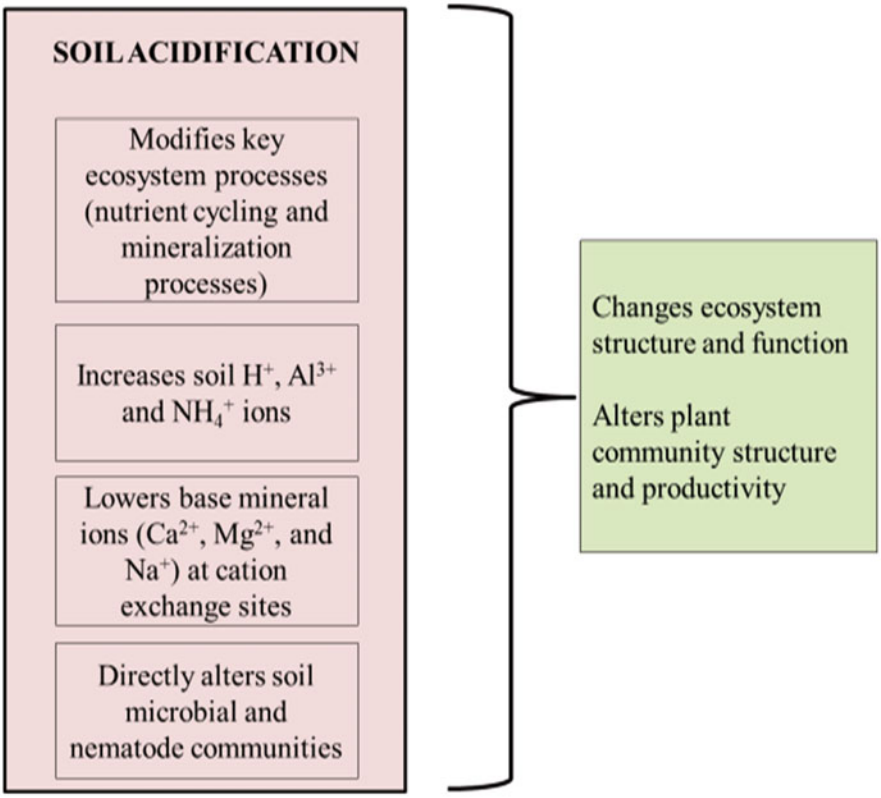

Fig. 1.6 Effects of soil acidification on plant community structure through various pathways

Zarfos et al. (2019) surveyed soil and understory vegetation at 20 different watersheds in hardwood forests of Adirondack Park, New York. This northern temperate forest is typified with acidic soil (pH ranged from 2.96 to 4.56), mainly due to glacial scouring of granitic gneisses/metasedimentary rock and atmospheric depositions. The study showed a significant reduction in understory plant diversity and richness at places where soil pH is very low ($pH < 3$). Also, soil acidification alters the composition of plant communities.

1.5 Adaptive Strategies to Combat Soil Acidification

Soil acidification is becoming an issue in areas where soils are unable to buffer their decreasing pH levels (Kunhikrishnan et al. 2016). With the dawn of the industrial era, various S- and N-rich emissions from different sources led to acidic precipitations, which have caused the soil acidification. Other activities such as mining and metallurgical extractions also increase the input of acid produced by

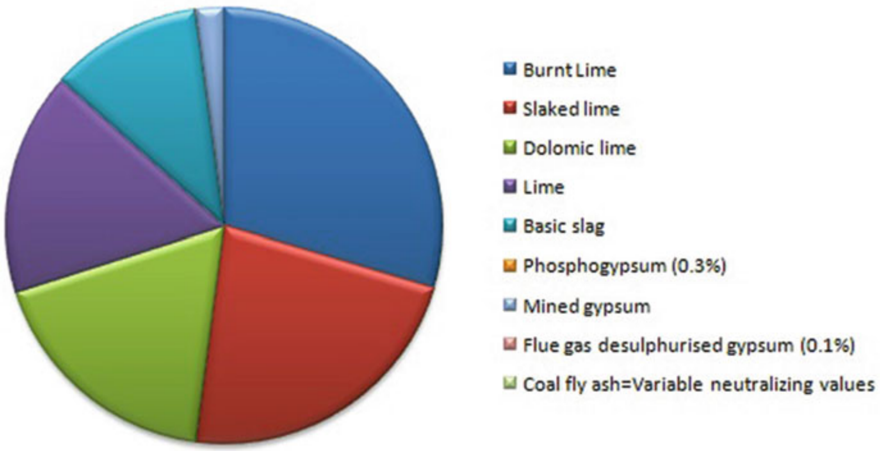

Fig. 1.7 Various liming materials and their neutralizing value expressed as weight percentage of pure lime (Modified from Bolan et al. 2003)

pyrite oxidation (Pal 2017). Such practices resulted into massive destruction and decline to flora and fauna of the affected regions. In the view of above, mitigation and management of acidic soil come into focus. To deal with the issue of soil acidification three major strategies could be adapted:

1. Decease the extent of H^+ ion generation,
2. Reducing the extent of the processes involved in H^+ and OH^- ions formation, and.
3. Countervail the produced acidity (Bolan et al. 2003).

These strategies could be implemented by the addition of some neutralizing materials into the soil.

Traditionally, addition of different forms of lime (Fig. 1.7) has been the most commonly used method to alleviate the acidification of the soil (Goulding 2016). However, the quantity of liming substances required for the acidity regulation depends on the buffering capacity of soil and the neutralizing value of liming substances (Fig. 1.7).

Apart from general liming materials, substances having Ca-containing liming potential such as phosphate rock, gypsum, fluidized bed boiler ash, and fly ash are also used for rectifying soil acidity (Dalefield 2017). Phosphate rocks are composed of two substances, viz. free calcium carbonate ($CaCO_3$) and apatite as phosphate minerals (Goulding 2016). Phosphate rocks have liming potential due to available free $CaCO_3$ and the H^+ ion-consuming capacity of apatite reduces the soil acidity. The $CaCO_3$ part of phosphate rocks dissolves rapidly and provides immediate response for soil acidity; while, apatite is a slowly dissolving substance, which makes the phosphate rocks last for a longer time (Zapata and Sikora 2002). Flue gas desulfurization (FGD) and gypsum ($CaSO_4.2H_2O$) are also used as soil amendments against soil acidity. The moderate solubility of FGD gypsum in water (solubility 2.5 g L^{-1}) makes it a good source of Ca^{2+} and SO_4^{2-} in the soil. Furthermore, it is also used to rectify the subsoil acidity and alkalinity of the soil (Walia and Dick 2016; Zhang et al. 2016).

The second widely used soil acidity neutralizing substance is alkaline stabilized biosolids, i.e., rice husks, animal manures, wood ashes, litter, and peat (Bolan et al. 2003; Behak 2017). These are widely used in the agricultural area as a substitute for inorganic amendments such as lime, limestone, coal ashes, cement, and lime kiln dust (Okagbue and Yakubu 2000). Alkaline-stabilized liming substances are recommended to increase the soil pH to 6.5 and more by the United States Environmental Protection Agency (Bolan et al. 2003).

Apart from conventional soil acidity neutralizers, biochars are also used in decreasing soil acidification. Biochars are produced from the pyrolyzed feed stocks ranging from lignocelluloses to manure at varying temperatures between 200 and 700 °C. The general properties of biochars include (i) soil acidity regulation by carbonates, silicate, alkaline oxides, and functional oxygen groups and (ii) soil nutrient pool maintenance by supplementation of macronutrients (N, P, K, and Ca) and micronutrients (Cu and Zn). Moreover, the high cation exchange capacity of biochar helps in nutrient retention in the soil (Dai et al. 2017). The properties of biochar vary with variability under the conditions of the product. For instance, Lehmann and Joseph (2015) reported that the pH of the biochar produced at 300–399 °C was 5.0, while its production at 600–699 °C showed a pH of 9.0.

Biochars can be used in waste disposal, energy production, climate change mitigation, and they also show positive responses on soil pH because of their alkaline nature and high pH-buffering capacity. It is also known to decrease the bioavailability of Al and alleviate its toxicity in acidic soil (Dai et al. 2017). However, the major drawback of using biochars on a large scale is its production cost and loss of huge portion of feedstock. Above all, moderation of soil acidification could only be achieved by minimizing the anthropogenically induced emissions and afforestation (Hong et al. 2018).

1.6 Conclusions

Soil is an interface that adjoins the atmosphere, lithosphere, hydrosphere, and biosphere. Acidification of soil thus has potentiality to alter the entire ecosystem structure and functions. Atmospheric depositions of nitrogen, sulfur, carbon dioxide, and other constituents, discharge of effluents and solid wastes, weathering of parent materials having acidic constituents, intense agricultural practices, and high precipitation are the major drivers of soil acidification. Lowering of the pH causes deterioration of soil fertility, loss of soil aggregate stability, and reduced soil biological activities due to metal toxicity. Terrestrial and aquatic habitats are negatively affected by constantly leaching of important basic cations (Na^+, Ca^{2+}, Mg^{2+}, and K^+) and increased solubilization of toxic metals (Al^{3+}, Cr^{2+}, Cd^{2+}, and Pb^{2+}). Soil flora and fauna are the organisms, which undergo a direct influence of soil acidification. Alteration in the soil properties due to soil acidification affects the growth, development, and productivity of crop plants, which invariably affects the countries' economy. The plant community structure pattern is an essential parameter to assess the change due to soil acidification. Atmospheric depositions (N and S) cause cuticle dissolution and inadequate availability of essential nutrients affect the plant species richness and their productivity. For the amelioration of acidified soil, different soil amendments are used such as lime, phosphate, and bio-wastes. However, advanced modification of flue stack, proper pretreatment of wastes, and afforestation are the most environmentally viable methods to combat the soil acidification.

Acknowledgments The authors are thankful to the Head, Department of Botany, the Coordinator, Interdisciplinary School of Life Sciences, DST-FIST, UPE, DST-PURSE, and CAS in Botany, Institute of Science, BHU, Varanasi. Durgesh Singh Yadav and Bhavna Jaiswal are thankful to the University Grants Commission, New Delhi for the financial assistance in the form of JRF and SRF. Meenu Gautam is thankful to the Council of Scientific and Industrial Research, New Delhi, for the financial aid in the form of Research Associateship.

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