Acid soil: Unwanted but unavoidable consequences of natural processes

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Abstract

Acid soil is a condition where the pH scale of the soil is less than 7. Most of the basic cations present in the exchange site of the soil have been replaced by the H+ ion from different sources. It is widely belief that different natural processes take part in soil acidification. But with human intervention the process of soil acidification is accelerated making the soil unfit for crop production. With increase in acidity of soil there is a decrement of most of the macro nutrient present. Activities of different beneficial microorganisms have been hampered. Solubility of heavy metal increases making vulnerable to certain human disease. Soil acidity can be determined by the activities of H+ in the soil solution which is called as pH. Soil pH is one of the most important attributes for soil quality point of view, which greatly influence different soil chemical reactions and processes. Among the types of soil acidity, active and exchangeable acidity has significant effect in soil health and activities of different microbial population. So, neutralizing acid soil is confined to only active acidity and some part of exchangeable acidity. For, ameliorating acid soil there are many management practices. Among them liming is considered most important. Different liming materials are present which produced OH- during hydrolysis reaction in the soil, and this OH- ion neutralised the H+ ion which were initially present in the soil or as a by-product of Al hydrolysis. For a proper soil health, soil acidity management is very important for sustainable crop production. So, understanding different process of soil acidification is a need for proper management.

Introduction

Soil acidification is a natural process where the pH of the soil is less than 7 (which is considered as neutral pH). It is a serious problem in many parts of the world affecting agricultural production and its gross income (Hajkowicz and Young, 2005). It is an increase in based neutralising capacity or decrease in acid neutralizing capacity leading to the decrease of soil pH by increasing acid strength in soil. Soil acidification in aerated soil will produced different acid, which in turn affect the ions uptake by different plants, ultimately deteriorate the growth of the plants both in natural and cultivated ecosystem. An acid soil can be defined as a base unsaturated soil which has large number of exchangeable H+ ions in the exchangeable clay lattice, making the soil a pH lower than 7. Soil acidity can be determined by the activities of H+ in the soil solution. It can be accelerated by certain activities of plants and animals disturbances and also can decrease by proper management practices (Bolan et al., 2005). Soils of different region have considerably different acidity
or lower pH value and occupy sufficient region in the world (Sumner and Noble, 2003). Soils developed from acidic parent material like granite will acidify the soil very fast than the soil developed from basalt (basic parent material) (Thomas and Hargrove, 1984). Soil acidification of surface soil (up to 30 cm) profile takes place due afforestation or conversion of pasture land to forest land leading to lower pH in soil with low basic cations (Berthrong et al., 2009). Different coniferous pine forest in the north eastern region of India possess low pH values with high aluminium (Al) toxicity because of its climatic condition (high rainfall) and low basic cations return to soil through pine litter. In cultivated soil causes of soil acidification is quiet common due to high cations present in the soil, inclusion of different leguminous crop in crop rotation cycle and use of different acid forming fertilizers. Generally plant absorbed more cations than anions from the soil to neutralised organic acid synthesis (Rengel and Tang, 2003). When root absorbs cations from the soil, equilibrium has to be maintained by releasing certain protons from the root which ultimately increase the acidity of soil. Legumes can uptake large number of cations from the soil (Rengel and Tang, 2003) than any cereals and also it can fixed nitrogen from the atmosphere leading to more soil acidification (Haynes, 1983), because during mineralisation process of the legume biomass, certain proton (H⁺) are released in the soil. Soils developed from different parent materials possess different pH value. Based on the parent material from where the soil has developed texture of a soil varies from other. Due to low in buffering capacity of sandy soil it will be very easy to acidify or rapidly acidify than a clayey soil.

An acid is a substance that donates protons (H⁺) to some other substances. In contrary to this a base is any substance that accepts protons (H⁺) or donates OH-. Soil acidity is expressed in terms of pH scale which gives the value of H⁺ activities in the soil solution. Soil pH is one of the most important attributes for soil quality point of view, which greatly influence different soil chemical reactions and processes (Bolan and Kandaswamy, 2005). It gives an important measurement, for deciding whether a soil is acidic or basic. It can be expressed as negative (-) log of [H⁺] activity (Activity = concentration x activity coefficient). Each unit change in soil pH is equivalent to a ten-fold change in the amount of acidity and basicity, as proposed by the Danish Chemist, Sorenson in 1909. The ranges of pH in soil are given in Fig. 1. With different pH value in soil, the acid forming cations concentration also differ, which gives the buffering capacity. In pH range of 2.4 to 3.8, iron (Fe) gives the buffering action in the soil. In this range of pH, maximum concentration will by occupy by iron. Similarly in pH range of 3.0 to 4.8 both iron (Fe) and aluminium (Al) are present. Different cations exchange properties of soil is maximum in the pH range of 4.2 to 5.0. And, above pH 5.0, silicates and carbonates occupies the exchangeable site of soil (Fig 1) (Sparks, 2003). Soil pH measures the activity of H⁺, which are actively participating in the soil solution, which we called as active acidity, and some parts of exchangeable acidity, but does not measure the potential acidity. A soil solution having pH value 7 is considered as neutral whereas pH value of >7 as basic soil and <7 as acid soil. Soil acidity rose due to the present of higher concentration of hydrogen (H⁺), aluminium (Al³⁺), Iron (Fe³⁺) and Manganese (Mn²⁺) in the soil solution and in exchangeable site of the clay lattice. There is a significant effect of soil pH on different beneficial processes taking place in soil. pH is considered as an important variable affecting the growth of beneficial microorganisms (Kunhikrishnan et al., 2016), which controls the carbon (C) and nitrogen (N) cycle
Soil acidifications restrict the growth of certain nitrifiers resulting low mineralisation process with nitrogen deficiency in soil (Robertson and Groffman, 2015). Most importantly the availability of nutrients in the soil is largely depends on soil pH. The cation exchange capacity (CEC) is also depends on the activity of H⁺ ions in the soil, which is a very important process in soil for plant nutrients availability. With decrease in pH of soil the solubility of certain acidic cations (Al, Fe and Mn) increases which can be toxic to plant roots. As pH increase the solubility of these cations decreases and started precipitation which decrease its effect. Activities of different microorganisms in soil also depend on pH of the soil. Population of fungi increases in lower pH than bacteria and other beneficial microorganisms (Vylkova, 2017). One of the most important problems faced by farmers while growing crops under low pH (soil acidity) is aluminium toxicity. In susceptible crops Al can reduce both the root and shoot growth retarding the production. In low pH, solubility of different heavy metals also increases which leads to the heavy metal contamination to the soil. So, understanding soil acidity and its management is very important for proper crop management practices.

![Fig. 1 pH ranges in soil and its buffering cations](image)

Types of soil acidity

Soil acidity can be classified into three types, namely (i) active acidity, (ii) exchangeable and (iii) reserve acidity.

Active acidity may be defined as the acidity developed in soil by the hydrogen (H⁺) and aluminium (Al³⁺) ions in soil solution (Fig. 2). Especially the H⁺ in the soil solution represent the active acidity. The concentration of both the cations are depends on the cation exchange site present in the soil (Sparks, 2003). Both the concentration of H⁺ and Al³⁺ ions in the soil solution is very small for active acidity. So, only a small amount of lime will be required to ameliorate the active acidity. But it is the most important type of soil acidity of its
interaction with the microorganisms and plant root rhizosphere. Most of the H⁺ in the solution is controlled by the Al³⁺ by its hydrolysis process. Active acidity directly influences the growth and development of both plant and microbes present in the soil (Bolan, 2003). There lies a dynamic equilibrium between the types of soil acidity. The measurement of pH is mostly confined to the active acidity of soil solution.

Exchangeable acidity is the acidity developed by hydrogen (H⁺) and primarily aluminium (Al³⁺), which are present/adsorb in the exchange site of clay lattice (Yu, 1997) (Fig. 2). When pH of the soil falls below 5.0, aluminium are present mainly in the form of Al³⁺, which than hydrolysed to to formed other species like ALOH⁺², Al(OH)₂⁺, Al(OH)₃ and Al(OH)₄ (Abdulaha-Al Baquy et al., 2018). Its quantity depends on the types of clay minerals and the amount of basic cations attached in the exchange site of the clay minerals in the soil (Thomas and Hargrove, 1984). During the process of soil genesis, exchangeable acidity takes part in the acidification of soil by deteriorating exchange surface of the soil. Aluminium present in 2:1 clay lattice got destabilized during hydrolysis of clay structure contributing to the exchangeable acidity. The concentration of hydrogen (H⁺) and aluminium (Al³⁺) are very high in a strongly acidic soil, which contribute to the exchangeable acidity. In strong acidic soil the basic cations present in the exchange site decreases with increase in the acidic cations (H⁺ and Al³⁺), making the pH of the soil drops to 4.0 and less. The magnitude of this exchange acidity is very high. Exchangeable acidity contributes some parts of Reserve/potential acidity which includes some weak organic acids, ionized acid functions and easily exchangeable cations (Sparks, 2003). Exchangeable acidity depends on the cation exchange site of the soil. The ration of exchangeable to total acidity is highest for the 2:1 type of clay (montmorillonite), medium for vermiculite and least for 1:1 type kaolinite.

Reserve acidity is that types of soil acidity which are present in the form of aluminium hydroxyl ions and non-exchangeable hydrogen (H⁺) and aluminium (Al³⁺) ions that are bound in organic matter and in between different silicate clay lattice structure that are not exchangeable (Blake, 2005) (Fig. 2). In soil, after neutralizing active and exchangeable acidity the remaining acidity is the reserve acidity. The magnitude of reserve acidity is much higher than the active and exchangeable acidity, requiring huge amount of lime to neutralise the reserve acidity. So, it is not worthy and necessary to attempt to neutralise the reserve acidity. Liming is always confined to neutralise the active and some parts of exchangeable acidity. Also, for measuring soil acidity using pH scale the acidity is restricted to active and some parts of exchangeable acidity (Sparks, 2003).
Source of soil acidity

Acidity in soil is caused by the adsorbed exchangeable $\text{H}^+$ and in the soil solution. So, any process in nature or human activities that contributes $\text{H}^+$ to the soil can be considered as a source of soil acidity. Following are the most important processes related to soil acidification (Fig. 3).

**Rainfall/Precipitation**

Acidic soil are mostly confined to the region where rainfall is high enough to leached down the easily soluble basic cations from the soil to the water table making the soil high in acidic cations with low solubility such as Fe and Al (Li and Hayes, 2017). These compounds when hydrolysis it can produce numerous quantities of $\text{H}^+$.
which is the main cause of soil acidity. Also, the main source of acidity in nature is carbonic acid which is formed by the combination of water (H₂O) and carbon dioxide (CO₂) both in atmosphere and beneath soil. The pH value of rainwater in equilibrium with atmospheric carbon dioxide is 5.6. When atmospheric CO₂ and rainwater combined, it gives carbonic acid and dissociates into bicarbonate and a proton (H⁺) (Eq 1). The proton that are released will replace the basic cations (Ca²⁺, Mg²⁺) which are initially present in the exchange site of the soil. The replaced basic cations will leach from the surface soil to the water table or to the deeper depth along with the rainwater making the soil acidic in nature.

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \quad \text{(Eq 1)}
\]

**Acid Precipitation/acid rain**

Natural source of acid precipitation includes volcanic eruption, production of nitrogen oxide during lightning etc. During volcanic eruption different compounds are produce in the atmosphere when react with rain water it produced certain acidic substance which contributes to soil acidity. Due to different anthropogenic activities (combustion of fossil fuels, industry, internal combustion engine exhaust etc.) there is an increase of acid precipitation which ultimately increases soil acidity (Sparks, 2003). Large part of acid precipitation occurs due to the emission of oxides of sulphur (S) and nitrogen (N). These compounds when react with the rain water it can convert into sulphuric acid and nitric acid (Eq 2 and 3), which are highly acidic in nature and can decrease the soil pH (Bolan et al., 2003).

\[
\text{2SO}_2 + \text{O}_2 \rightarrow \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ \quad \text{(Eq 2)}
\]

\[
\text{2NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2 \rightarrow \text{NO}_3^- + \text{H}^+ \quad \text{(Eq 3)}
\]

**Different processes in nitrogen (N) cycle**

The process by which the N in organic matter gets converted into available form of ammonium and nitrate is called mineralization. The process of mineralization includes different steps like aminization, ammonification and nitrification. Atmospheric nitrogen is mainly transferred to the soil by plant fixation and this accumulation of N in organic matter is a source large number of proton (H⁺) during the mineralization of these organic nitrogen to inorganic form. Among all the mineralization processes, nitrification contributes 2 molecules of proton (H⁺) in the soil contributing soil acidity (Eq 4). Nitrification in acid soil can leads to more acidification and toxicity cause by Al and heavy metals (He et al., 2012). Nitrification process increases the NO₃⁻ concentration in soil with higher chances of leaching (Wrage et al., 2001). So, with NO₃⁻ leaching from the soil there is reduction of certain basic cations as ion pairs resulting soil acidification. Also during the assimilatory nitrogen fixation process by plants an H⁺ produced to the soil making soil acidity (Eq 5). During N cycle process, N from the soil will transferred to the atmosphere mainly due to ammonia volatilization and denitrification processes. Ammonia volatilization is the chemical process where the ammonium (NH₄⁺) from mineralization process or from applied fertilizer is converted into ammonia gas due to high temperature and pH. During this process a hydroxyl (OH⁻) ion is used for converting the NH₄⁺ to NH₃, contributing to soil acidity (Eq 6).
NH₄⁺ + 2O → NO₃ + H₂O + 2H⁺  -------------------------- (Eq 4)

NH₄⁺ + R-OH → R-NH₂ + H₂O + H⁺  -------------------------- (Eq 5)

NH₄⁺ + OH⁻ → NH₃ + H₂O  -------------------------- (Eq 6)

Acid forming fertilizers

Nitrogenous fertilizers like ammonium sulphate and ammonium nitrate are acid forming fertilizers. When these types of fertilizers are applied to the soil ammonium (NH₄⁺) will replace the basic cations (Ca, Mg, K and Na) initially present in clay lattice and leached down to the water table (Hedley and Bolan, 2003). The applications of N fertilizers also produce H⁺ to the soil by two processes of nitrification and nitrate (NO₃⁻) leaching. Nitrate is highly soluble in water and its leaching loss is quite common during heavy precipitation. During nitrate leaching loss, depletion of different basic cations (Ca, Mg, K and Na) takes place as ion pairs contributing to the soil acidification process. Application of urea (most common N fertilizer) also contributes H⁺ to the soil. During urea hydrolysis two moles of NH₄⁺ ions is produced which on nitrification and volatilization process contributes to soil acidity (Ozlu and Kumar, 2018). A decrement of pH in the tropical acid soil was observed with the used of three nitrogenous fertilizers in the order of ammonium sulphate > urea > ammonium nitrate (Stumpe and Vlek, 1991). Single super phosphate (SSP) is the most common phosphorus fertilizer used containing mono calcium phosphate as the primary phosphorus component. When this monocaicium phosphate dissolve in the soil it will give di calcium phosphate with the released of phosphoric acid, which consequently dissociates into phosphate anions (H₂PO₄⁻) and H⁺, contributing to soil acidification.

Anthropogenic activities

Human activities like afforestation, coal mining, tillage practices (land disturbance), leguminous cropping systems etc. lead to the soil acidification. During coal mining and any land disturbance pyrites (FeS₂) is commonly associated. So, exposure of pyrites to the soil atmosphere will leads to the oxidation process and releasing extremely acidic water to the soil (Sparks, 2003). Different microorganisms are responsible for the oxidation of pyrite in soil. Especially in acid soil Thiobacillus thiooxidans and T. ferrooxidans are predominantly responsible. In a very low pH condition, the oxidation of pyrite is extremely slow, which a pH-sensitive process. During any anthropogenic activities certain soil structure is deteriorated leading to the release of certain acid forming cations (Fe, Mn, and Al) to the soil. During hydrolysis process of the cations large number of H⁺ are produce to the soil making more acidic.

FeS₂ + Fe³⁺ + H₂O → Fe(OH)₃ + H₂SO₄

Fe³⁺ + 3H₂O → Fe(OH)₃ + 3H⁺  --------------------------(Eq 8)

Al³⁺ + 2H₂O → Al(OH)₂ + 2H⁺  --------------------------(Eq 9)

So, from equation 7, due to high concentration of sulphuric acid developed from the exposed pyrite, the pH of the soil can reach up to 2.0 in coal mining area and can be <4 in acid sulphate soils. The
highly acidic sulphuric acid, when meet with the drainage water or flood water can transport to different places dissolving different clay minerals in the soil which released soluble Al. And this Al during hydrolysis process will supply $H^+$ to the soil contributing soil acidity (Eq 9). With cultivation practices the cations present in the soil increases. It has been reported that different crops absorbed more cations than anions from soil. Especially legumes extract more cations than any cereals (Rengel and Tang, 2003). When leguminous roots absorbed cations from the soil, equilibrium in the soil has been disturbed. So, to maintain the equilibrium certain protons are released from the legume which contributes to soil acidification (Lesturjez et al., 2006). Land use change is also one of the important human activities which increase the soil acidity. Under temperate region, land use change of pasture or grassland to forest leads to the reduction of pH in soil (Parfitt et al., 1997). Nonetheless, the influence of different land use change on soil acidification depends entirely on the proton ($H^+$) fluxes.

Parent materials

Some soils have developed from parent materials which are acidic in nature. Of these the most important is granite and this may contribute to soil acidification, due to the present of excess silicic acid. Soils that have developed from different parent materials have different ability to accumulate organic matter (Heckman et al., 2009). Also, depending on the parent materials of the soil which has developed will have different soil texture (sand, silt and clay) as well as the content of amorphous iron (Fe) and aluminium (Al). In soil aluminium (Al) mainly present in the clay minerals of 1:1 and 2:1 octahedral sheet, which depends on the parent materials from where the soil has been developed. Also, it is present in the soil as crystalline or amorphous form of oxides and hydroxides (van Ranst et al. 2017). $Al^{3+}$ from the octahedral sheet is replaced by the $H^+$ which is very reactive in soil and can produce large number of $H^+$ ions during hydrolysis process increasing soil acidity (Yu 1997). So, depending on parent material of the developed soil, pH of soil varies. Soil with high percentage of clay have high buffering capacity with high resistance to change in pH of the soil, whereas in sandy soil due to low buffering capacity there can be a drastic change of pH with little source of acid to the soil.

Management practices

To minimized the rate and impact of soil acidification certain management practices can be perform with an aim to reduce or minimizes the rate of $H^+$ generating processes and neutralised the acidity produced. Soil acidification is generally a natural process but with certain human activity this process is increasing. In a well-managed and controlled condition soil acidification or the rate of acid generation can be altered by using basic fertilizer, reducing pollution level (C, N and S) in the air, minimising $NO_3^-$ leaching, preventing surface soil erosion, avoiding use of acid producing fertilizer, selecting crops which can withstand acid soil (Wortmann, 2014). Among all the practices to ameliorate soil acidity the most common one is liming (Athanase et al., 2013). Liming is a vital and most effective practice to ameliorate soil acidity constraints and improve production of crop on acid soils. Sometimes lime is considered or named as foundation of crop production or ‘workhorse’ in acid soils (Fageria and Baligar, 2008). Other than neutralizing the soil, liming also will
improve the physical, chemical, biological and fertility of the soil with immobilization of toxic substance present in the soil (Nduwumuremyi et al., 2013). Different liming materials are available, that includes calcite (CaCO₃), slaked lime (Ca(OH)₂), burnt lime (CaO), slag (CaSiO₃) and dolomite (CaMg(CO₃)₂). The quantity of these liming materials to neutralise the acid soil depends on the neutralizing value (NV) and pH buffering capacity of the soil (Kunhikrishnan et al., 2016). Also, lime requirement to neutralised a soil depends on certain other factors which includes quality of liming material, crop species, crop management practices, base saturation, initial pH of the soil, economic feasibility etc. Adding liming material to the agricultural soil reduced the nitrous oxide emission (N₂O) by limiting the nitrite (NO₂⁻) level in the soil which could produce N₂O by reduction process (Barton et al., 2013). Different range of alkaline materials (kiln dust, limestone, alkaline coal fly ash, wood ash etc) also can be used to neutralise the acidic soil. Different liming materials and alkaline materials that are used to ameliorate the acidic soil are to increase the pH up to 6.5. When liming materials are applied to the soil the solubility of the acid cations (H⁺, Fe, Al, Mn) decreases and increase the initially low concentration of the basic cations (Ca, Mg, K, Na) in the soil. The hydrolysis of the liming material takes place in the soil with the releases of OH⁻ thereby neutralising the H⁺ with a concomitant decrease of Al and Mn (Kunhikrishnan et al., 2016). Also liming provides cations (Ca and Mg) which are basic in the soil that reduced the solubility of heavy metals.

\[
\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \quad \text{(Eq 10)}
\]

The OH⁻ produced in the above reaction will react with the H⁺ initially present in the soil or the product of hydrolysis process of Al³⁺ and Fe³⁺. The overall reaction can be depicted as follow.

\[
\text{Al-soil} + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca-soil} + \text{Al(OH)}_3 + \text{CO}_2 \quad \text{----------------------- (Eq 11)}
\]

**Conclusion**

Soil acidification is an unwanted natural phenomenon caused by certain processes occurring in nature, like rainfall, acid precipitation, nitrogen cycle, sulphur cycle etc. With the inclusion of certain anthropogenic activities (fossil fuel burning, clearing of vegetation, soil disturbance, coal mining etc.) the acidification of soil has been accelerated. But with managed soil condition the acidification process can be minimised. This acidification of soil leads to loss or deterioration of soil health which is important for proper crop production. With the decrease in pH or increase in acidification most of the macro nutrients availability decreases and solubility of heavy metals increases. So, it is of great important to manage the acid soil for improving soil health and reduce the heavy metal contamination. Management practice of acid soil includes liming the soil which has been traditionally practiced with certain liming materials to reduce the H⁺ concentration in the soil as well as to improve the basic cations. Certain other management practices are there with an aim to reduce H⁺ in the soil solution that includes reducing surface runoff, minimizing air pollution, reducing land use change, balance use of both acid and basic fertilizers etc.
References


