Nutrient and Water Use Efficiency in Soil: The Influence of Geological Mineral Amendments

Binoy Sarkar and Ravi Naidu

Abstract

Mineral amendments are known to improve the physical, chemical and biological properties of soil, which in turn can enhance the efficiency of nutrient and water use by plants. This chapter discusses the current state of the knowledge regarding the application of geological mineral amendments in soil which either helps to retain nutrients in soils or prevents losses of nutrients from soil and directly or indirectly contributes to improve the overall nutrient use efficiency (NUE). A critical analysis of the currently available research information recommends a site-specific (precision) management approach in order to explore the most beneficial effects of the mineral materials for increasing plants' nutrient and water use efficiency. The management practices should include an integrated plant nutrition system (IPNS) for the best utilisation of resources including mineral materials, fertilisers and organic inputs. This holds the potential for leading to a reduced fertiliser input in modern agriculture and therefore may lower the cost of agricultural production without impacting the crop yield.

Keywords

Nutrient use efficiency • Mineral amendments • Integrated plant nutrition system • Agricultural production

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1 Introduction

Numerous agricultural soils in the world are inherently deficient in one or more essential nutrients which are required as part of a sustainable crop production system. In the current era where scientific developments are being made almost weekly, the most intensive farming systems ever known are being introduced to

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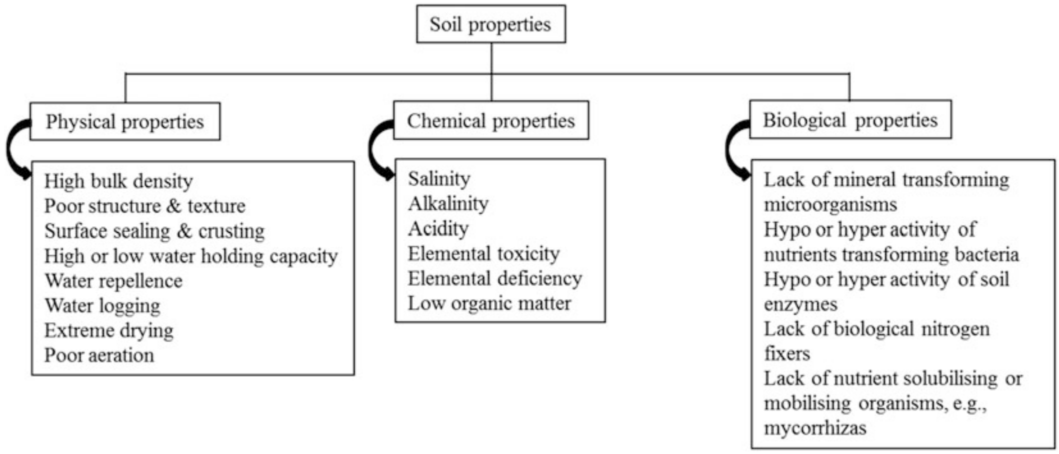

Fig. 1 Soil properties which directly or indirectly reduce NUE by plants

meet the food requirements of the growing global population, which is projected to reach between 8.3 and 10.9 billion by 2050. However, intensive cultivation systems invariably lead to numerous soil degradation issues (e.g. salinity, acidity, alkalinity, erosion, pollution and water scarcity). Numerous natural and synthetic inputs including chemical fertilisers have been successfully applied as part of best practice for improving soil fertility and productivity. Amongst the numerous inputs, chemical fertilisers are one of the most expensive items commonly used by farmers in order to increase crop yields. However, the recovery and utilisation of applied nutrients by plants in many soils is generally low. It has been estimated that the overall efficiency of applied fertilisers is approximately 50 % or lower for N, less than 10 % for P and 20–40 % for K (Baligar and Bennett 1986a, 1986b). Losses by different processes such as leaching, run-off, gaseous emission and fixation by soil are the significant factors that lower the use efficiencies of the applied nutrients (Baligar et al. 2001). These losses not only lower the crop yields, but they also contribute to potential soil degradation and can impair the local water quality (Baligar et al. 2001). Therefore, this chapter discusses the current state of the knowledge regarding the application of geological mineral amendments in soil which either helps to retain nutrients in soils or prevents losses of nutrients from soil and directly or indirectly contribute to improve the overall nutrient use efficiency (NUE).

2 NUE and Soil Properties Affecting It

Several authors have discussed the topic of plant NUE (Epstein 1972; Vitousek 1982; Blair 1993; Baligar et al. 2001; Hawkesford 2011). The NUE is defined as the ability of a genotype/cultivar to acquire nutrients from growth medium and/or to incorporate or utilise them in the production of shoot and root biomass or utilisable plant material (e.g. seed, grain, fruit and forage) (Blair 1993). Under heterogeneous environmental and ecological conditions, the genetic and physiological traits of a crop plant primarily control its NUE. Furthermore, numerous soil properties directly or indirectly affect the NUE by plants (Baligar et al. 2001). Soil properties encompass a range of physical, chemical and biological factors (Fig. 1). By applying geological mineral amendments to the soil, many of these properties can be enhanced or repaired, which results in improved NUE by plants.

Table 1 Use of mineral amendments for retaining nutrients in compost materials

Mineral	Compost type	Nutrients form retained	Retention mechanism	References
Pyrite	Phosphocompost	NH_4^+-N and P	pH reduction reduces NH_3 volatilisation	Bangar et al. (1988)
Alum	Swine manure compost	NH_4^+-N	pH reduction reduces NH_3 volatilisation	Bautista et al. (2011)
Clinoptilolite	Swine manure compost	NH_4^+-N	Zeolite exchange sites adsorb NH_4^+-N	Bautista et al. (2011)
Clinoptilolite and sepiolite	Pig slurry and wheat straw compost	NH_4^+-N	Zeolite exchange sites adsorb NH_4^+-N	Bernal et al. (1993)
Clinoptilolite	Municipal solid waste compost	NH_4^+-N	Zeolite exchange sites adsorb NH_4^+-N	Gamze Turan and Nuri Ergun (2007)
Clinoptilolite	Cattle manure applied to soil	NH_4^+-N and NO_3^--N	Zeolite exchange sites adsorb NH_4^+-N and render it unavailable to nitrifying bacteria; NO_3^--N leaching is therefore reduced	Gholamhoseini et al. (2013)
Goethite, gibbsite and allophane	Poultry manure compost	Potentially mineralisable N	Clay materials stabilise C in the composts	Bolan et al. (2012)

3 Geological Mineral Amendments

The amendment of soils with geological minerals can directly or indirectly influence the nutrient transformation, nutrient retention, nutrient losses, water retention and their use by plants. Table 1 summarises a number of examples of geological mineral amendments which are used to retain nutrients in composted materials, which improve crop NUE post application. The most commonly used mineral amendments to soils include clay minerals, zeolites, calcite and dolomite, gypsum, phosphate rock, pyrite, alum, waste mica and mineral mixtures in some other industrial by-products (e.g. fly ash and red mud).

3.1 Clay Minerals

Water holding capacity (WHC) is an important factor which affects nutrient chemistry and, hence, availability to plants. Light-textured soils usually have poor WHC. In some parts of the world, especially in arid or semiarid regions, soils can become water repellent due to capping of the soil particles by some hydrophobic organic compounds. In those soils, the application of clays or clay-rich subsoils, commonly known as ‘claying’ or ‘clay spreading’, has been reported to be very effective in adequately preserving the soil moisture for crop production. The clay is spread over the organic coated sand grains, masking the hydrophobic sand surface and exposing a hydrophilic clay surface (Ward and Oades 1993; Cann 2000). Approximately 43 years ago, Clem Obst, a South Australian farmer, accidentally discovered the ability of clays to counteract the effects of water-repellent sand (Cann 2000). More than 37,000 ha of land in South Australia is now clay spread, of which 32,000 ha is in the south-east of South Australia (Cann 2000). The application of clay to those soils has improved the nutrient and moisture retention in the topsoil, the germination, the establishment and yield of pasture plants and crops and increased the effectiveness of preemergent herbicides (Cann 2000).

Claying (the addition of clay-rich subsurface soils) and deep ripping (breaking up the compacted soil layers using tines down to a depth of 35–50 cm to loosen hard layers of soil) in water-repellent sand plain soils improve water and nutrient retention and are therefore an effective long-term management technology for increasing crop NUE. The low organic carbon and clay content of sand plain topsoils results in poor nutrient-holding capacity (CEC < 3) (Hall et al. 2010). Research has shown that the effects of claying include increased concentrations of organic carbon by 0.2 %, potassium (K) by 47 mg kg^{-1} and cation exchange capacity (CEC) by 1.3 cmol (p^+) kg^{-1} in the topsoil (Hall et al. 2010), respectively. The authors reported that claying improved the yield of canola, lupin and barley by as much as 102 % in soils; however, it reduced the rainfall-limited yield potential of these soils to 30–50 % (Hall et al. 2010). The increase in yield was due to a combination of effects including higher plant emergence, improved plant nutrition (in particular K) and near surface water infiltration and distribution (Hall et al. 2010). Full yield potential could not be achieved due to higher soil strength as a result of the clay being applied. Deep ripping may increase the yield by 11–20 % (Hall et al. 2010). A time period of up to 6 years may be required before the combination of claying and deep ripping technologies fully overcomes the water-repellent nature of soils (Hall et al. 2010). The addition of beneficiated bentonite (bentonite saturated with Ca^{2+}, Mg^{2+} and K^+ in a ratio of 8:4:1) at a rate up to 40 t ha^{-1} to degraded Oxisol and Ultisol in tropical Australia permanently improved the basic surface charge which concomitantly caused a significant and sustained increase in forage sorghum yields on both the soil types (Noble et al. 2001). Similarly, acid waste bentonite (a by-product from vegetable oil bleaching) co-composted with rice husk, rice husk ash and chicken litter showed a highly significant increase in maize yields over two consecutive cropping cycles grown on a degraded soil in northern Thailand (Soda et al. 2006).

The increase in organic carbon contents of soil due to the application of clays occurs by the physical binding and protection of organic materials from microbial decomposition by the added minerals (Hall et al. 2010; Bolan et al. 2012; Churchman et al. 2013). The addition of goethite, gibbsite and allophane could potentially increase the half-life of poultry manure compost from 139 days to 620, 806 and 474 days, respectively (Bolan et al. 2012). The stabilisation of carbon in compost by clays was not reported to impair the quality of composts in terms of their ability to improve post-application soil quality parameters (e.g. potentially mineralisable nitrogen and microbial biomass carbon) (Bolan et al. 2012). Following application to soils, these clay-rich composts improve the organic carbon content of soil and reduce carbon loss as CO_2.

The water use efficiency of plants is closely related to the NUE and hence the crop yield. The application of clay to light-textured soils is known to improve the water use efficiency, growth and yield of crop plants (Al-Omran et al. 2005, 2007, 2010; Ismail and Ozawa 2007). Desirable crop performance can be obtained by applying clays to sandy soils which have poor irrigation utilisation efficiency. Remarkable improvement was achieved in cucumber and maize yields (2.5 times as compared to control) through improved water retention and water use efficiency when sandy soils were amended with a clay-rich soil which contained 21 % clay (Ismail and Ozawa 2007). Either by overlaying or incorporating methods (in top 20 cm depth), the clay application reduced water usage by approximately 45–64 % in areas under cucumber and maize cultivation (Ismail and Ozawa 2007). The water content distributions in the root zone area of squash (*Cucurbita pepo*) grown in sandy calcareous soils under surface, and subsurface drip irrigation was significantly improved by the amendment with clay deposits (Fig. 2), which provided a yield increment up to 13 % (Al-Omran et al. 2005).

Microorganisms play crucial roles in the cycling of nutrients in soils. Some specific microorganisms take part in nutrient transformation and make them available to the growing plants, and therefore, the NUE of plants is improved. The most widely used organisms are *Rhizobium* and *Bradyrhizobium* spp., which have the capacity to fix atmospheric N_2 into soil in a symbiotic relationship with leguminous plants (Elsas and Heijnen 1990). In addition to N

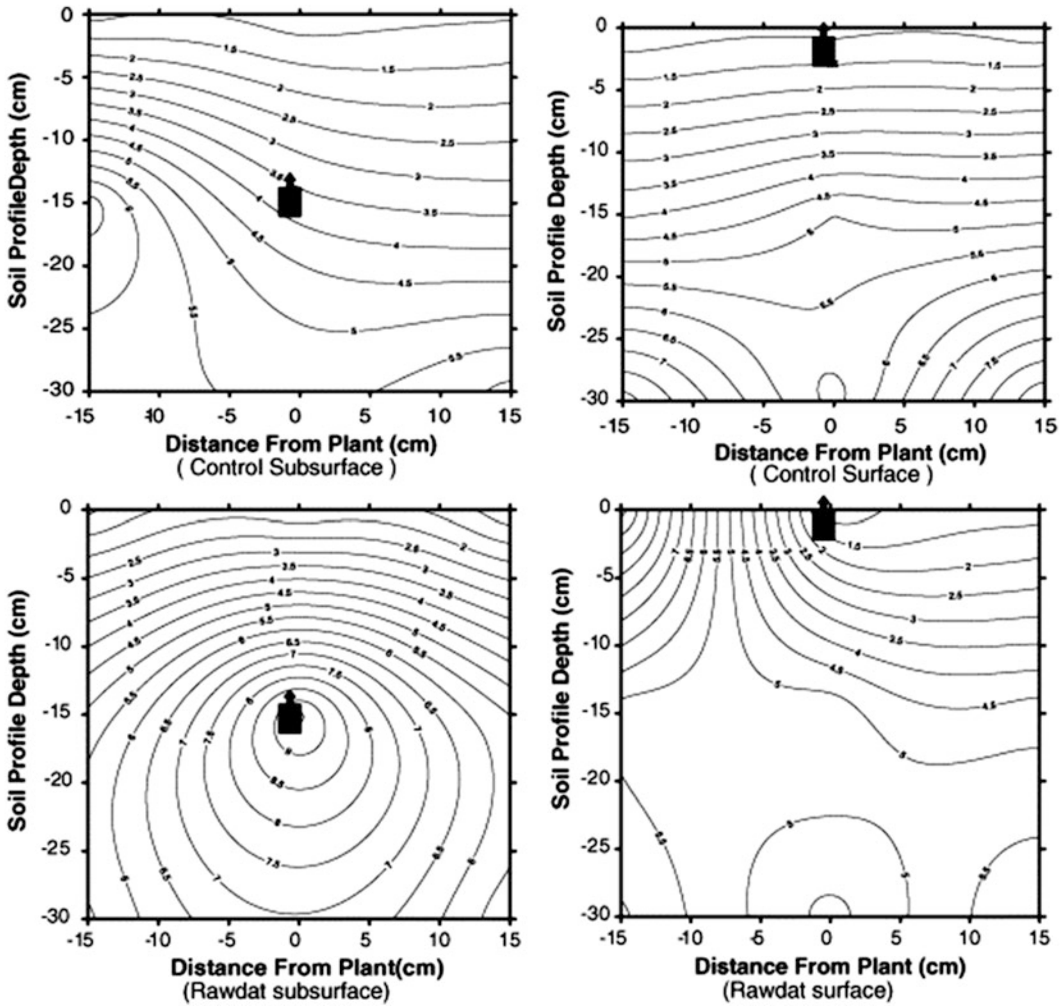

Fig. 2 Water content distributions in the root zone area of squash (*Cucurbita pepo*) grown in sandy calcareous soils amended with Rawdat clay deposit (59 % clay; high smectite content) under surface and subsurface drip irrigation. The control treatment contains no clay amendment. The *black rectangle* represents the position of the irrigation emitter (Al-Omran et al. 2005)

nutrition, the available P status of soils can also be improved by certain species of bacteria, for example, *Bacillus polymyxa*, *Bacillus megaterium* and *Pseudomonas fluorescens*. To obtain the optimum effect in desired nutrient transformation, an application method that facilitates the survival of a sufficiently high number of bacteria in the soils for a longer period of time is required (Elsas and Heijnen 1990; Heijnen and van Veen 1991; Heijnen et al. 1992). At an application rate of 5 %, bentonite clay was successful in improving the survival of *Rhizobium leguminosarum* biovar *trifolii* which was introduced into a loamy sand soil through creation of large amount of microhabitats which protected the bacterium from protozoan predation (Heynen et al. 1988; Heijnen and van Veen 1991). Provided the rhizobial culture and the clay were mixed thoroughly before introduction into soil, concentrations as low as 0.5 % bentonite improved rhizobial survival compared to a control without bentonite amendments (Heijnen et al. 1992). With the use of less clay, some deleterious effects of clay addition including excessive swelling of the soil could be avoided (Heijnen et al. 1992). The protective effects of clay on the survival of introduced bacteria in soil were the result of an increase in the number of pores (almost doubled) with an equivalent neck diameter <6 μm (Heijnen et al. 1993). The growth and survival of bacterial species including *Pseudomonas fluorescens* and *Bacillus subtilis,* which are known to improve soil available P, was also better supported in clay-rich fine-textured soil as compared to silt loam and coarser loamy sand soils (van Elsas et al. 1986).

3.2 Zeolites

The addition of zeolite in combination with pure organic amendments (e.g. cellulose) improved the nitrogen use efficiency in calcareous sandy soils under citrus cultivation (He et al. 2002). With the application of clinoptilolite and cellulose (both 15 g kg^{-1}), ammonia volatilisation from NH_4NO_3-, $(NH_4)_2SO_4$- and urea-treated soils (applied at the rate 200 mg N kg^{-1} soil) decreased by 4.4-, 2.9- and 3.0-fold, respectively, compared to soils without amendments (He et al. 2002). The organic input in the form of cellulose provided favourable conditions for microbial growth and increased the microbial biomass, which consequently caused N retention by microbial immobilisation. The mineral zeolite improved the N retention further by adsorption of NH_4^+-N in the ion-exchange sites. The interactive effect of cellulose and zeolite amendment was additive on soil microbial biomass which improved nutrient retention and availability of nutrients to microorganisms and citrus plants.

The application of zeolite along with cattle manure was shown to improve the N use efficiency directly in sunflower grown in sandy soils under semiarid conditions (Gholamhoseini et al. 2013). The treatment which combined urea, cattle manure and clinoptilolite (14–21 %) was considerably more effective than urea alone or urea with cattle manure with respect to improving the most quantitative and qualitative traits of sunflower (Gholamhoseini et al. 2013). Zeolites are usually reported to adsorb the NH_4^+-N contained in composts in their pores. The nitrifying bacteria, which use NH_4^+-N as the precursor for NO_3^- production, cannot access the zeolite pores (Gholamhoseini et al. 2013). Thus, zeolites render NH_4^+-N unavailable to the nitrifying bacteria and decrease the transformation of NH_4^+ to NO_3^-, hence preventing NO_3^- leaching. Since zeolite reduces N leaching in such conditions, it increases the plant-available N and consequently the N use efficiency. In addition, the application of clinoptilolite reduced P leaching; however, the effect was more prominent in reducing the N leaching (Gholamhoseini et al. 2013).

As a naturally occurring mineral, zeolite has the potential to stabilise nutrients in various compost materials (Bernal et al. 1993; Lefcourt and Meisinger 2001; He et al. 2002; Gholamhoseini et al. 2013). The degree of retention of NH_4^+-N by zeolites may vary depending on the pore diameter of these materials. For example, clinoptilolite has a higher capacity for water adsorption than phillipsite due to its larger pore diameter (Hayhurst 1978), and NH_4^+-N adsorption by zeolites is inversely related to water adsorption capacity (Bernal et al. 1993). In these materials, the adsorbed water blocks the internal channels against NH_4^+-N adsorption. Therefore, the effectiveness of zeolites in retaining NH_4^+-N, and consequently their optimum rate of application, is largely dependent on the water loss characteristics during the composting process.

3.3 Calcite and Dolomite

The application of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) as liming materials is well known for the management of acid soils (Haynes and Naidu 1998; Naidu et al. 1990a, b; Naidu and Syers 1992; Fageria and Baligar 2008). The application of lime increases the soil pH at which a negative charge on the surface clay colloids develops and a repulsive force between soils particles dominates (Naidu et al. 1990b; Haynes and Naidu 1998). It also causes an increase in both the Ca^{2+} concentration and the ionic strength in the soil solution. As a result, a compression of the electrical double layer occurs which promotes flocculation of the soil particles at a higher lime rate (Haynes and Naidu 1998). This improves the quantity and quality of organic matter, the soil structure and the congenial nutrient transformation in soils subsequently.

In addition, weathering of silicate minerals is a significant source of plant nutrients in soils. Bacteria primarily take part in this type of mineral weathering. Amendment with calco-magnesium mineral (liming) in mountainous forest soils (which typically have a high organic matter content and acidic pH) could improve the weathering rate of phyllosilicate minerals by bacteria compared to that in the unamended soils (Balland-Bolou-Bi and Poszwa 2012). The calco-magnesium mineral amendment increased the availability of some existing nutrients in the soils, which subsequently enhanced bacterial silicate mineral weathering potential (Balland-Bolou-Bi and Poszwa 2012).

The decline of forest vegetation due to anthropogenic acidification is a common problem in mountainous soils in Europe and elsewhere. The application of dolomite in those soils raises the pH and the concentrations of the base cations (Ca and Mg), which concomitantly decreases heavy-metal toxicity to plants (Ingerslev 1997). The diversity of the acidobacterial and gram-positive groups declines, and the diversity of the proteobacterial community improves, due to dolomite application to soils (Clivot et al. 2012). The ratio between *Proteobacteria* and *Acidobacteria*, which increases as a result of dolomite application, serves as a microbial indicator of soil quality improvement (Hartman et al. 2008; Clivot et al. 2012).

The application of calcite ($CaCO_3$) to soil as a liming material can result in long-term changes in the humus structure of soils. Soil humus can be classified into three types, namely, mor, moder and mull (Green et al. 1993). Mor is the type of humus which arise under conditions of low-biological activity in soil and contains a C:N ratio of more than 20 and sometimes 30–40. Moder is a transitional form of humus between mull and mor; it has a C:N ratio of 15–25. Mull is a well-humified organic matter, which is produced in biologically very active habitat and contains a C:N ratio of 10. After approximately 22 years of application, one study reported that the humus structure in calcite-treated forest soils receiving NPK fertilisers evolved from the 'moder' to the 'mull-moder' type as compared to the moder-type humus in control soils (Deleporte and Tillier 1999). This subsequently altered the soil faunal communities; the lumbricid population (epigeic species) in those calcite-treated soils increased (Deleporte and Tillier 1999).

3.4 Gypsum

Gypsum ($CaSO_4{\cdot}2H_2O$) is a key mineral material for maintaining agricultural production in soils affected by sodicity. The altered electron and proton activities (pE and pH) in sodic soils, which are produced as a result of a degraded soil structural environment, create nutrient constraints in such soils (Naidu and Rengasamy 1993). Upon application to sodic soils, gypsum increases the stability of soil organic matter, leads to the formation of more stable soil aggregates, improves water penetration into the soil and facilitates more rapid seed emergence (Wallace 1994). The application of gypsum is known to increase the growth and yield of numerous crops (e.g. wheat (Whitfield et al. 1989; Thomas et al. 1995), sorghum (Thomas et al. 1995), maize (Toma et al. 1999) and alfalfa (Toma et al. 1999)). Gypsum helps to improve soil structure by better flocculation and aggregation and rupture soil strength (Rengasamy and Olsson 1991; Rengasamy et al. 1993). The long-term effects of gypsum application to soils are the alteration of soil pH and increased amounts of exchangeable Ca and SO_4^{2-} (Toma et al. 1999). Soil pH plays a crucial role in the transformation of fertilisers in soils; the loss of NH_3 from nitrogenous fertiliser as a result of volatilisation is accelerated in an alkaline soil, and thus, the N use efficiency is reduced (Bolan et al. 2004). In such cases, the correction of soil pH which results from applying amendments can improve NUE by plants.

3.5 Phosphate Rock

The mineral constituents in phosphate rocks are generally apatites, crandallites, millisites, silica and calcite. Amongst these hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$) is considered as the most important P-containing mineral which can supply P to plants following direct application to soils. However, the agronomic effectiveness of phosphate rocks depends on many factors: (a) the chemical nature and physical form of the product, (b) soil properties, (c) type of crop species grown, (d) climatic conditions, and (e) method of measuring reactive P in phosphate rock and soil (Bolan et al. 1990; Chien and Menon 1995). The agronomic effectiveness is assessed against a standard P-supplying fertiliser (e.g. SSP) as shown below (Eq. 1) and referred to as relative agronomic effectiveness (RAE) (Bolan et al. 1990).

$$\mathrm{RAE} = 100 \times \frac{[(\text{Yield with phosphate rock}) - (\text{Yield in control})]}{[(\text{Yield with SSP}) - (\text{Yield in control})]} \quad (1)$$

Aluminium (Al) toxicity in acid soils and associated low P availability can be effectively addressed by direct application of phosphate rocks to soils (Easterwood et al. 1989; Rajan et al. 1996). This mineral amendment is ideally suited for long-term crops such as permanent pastures and plantation crops, but can show immediate seasonal effects in plants grown under acidic soil conditions (Rajan et al. 1996). Since depending on their sources phosphate rocks might contain significant amount of heavy trace elements, care should be taken for their direct application to soils for avoiding a potential heavy-metal build-up (Raven and Loeppert 1997).

The low reactivity of phosphate rocks (less plant-available P fraction) in certain soil types (neutral and alkaline) can be overcome by simple partial acidulation, co-composting and inoculation with microorganisms (Begum et al. 2004; Biswas and Narayanasamy 2006; Biswas et al. 2009; Biswas 2011). Microorganisms such as fungi including arbuscular mycorrhiza and P-solubilising bacteria have been proved to be efficient inoculant for increasing P availability from phosphate rocks both in soils and compost materials (Vassilev et al. 1995; Toro et al. 1997; Biswas and Narayanasamy 2006; Park et al. 2010).

3.6 Pyrite and Alum

Some mineral materials (e.g. pyrite and alum) have the ability to correct high pH and reduce nutrient loss from compost materials during their production and after application to soils. Approximately 33–62 % of the initial total N of manure may be lost during composting if some critical parameters (e.g. pH, moisture content and temperature) are not properly controlled (Kithome et al. 1999). The loss of N from phosphocompost enriched with nitrogenous compounds is significantly reduced by amending the compost with Fe-bearing mineral (e.g. pyrite (FeS_2)) (Bangar et al. 1988). Since a high pH value promotes N loss through NH_3 volatilisation, the role of pyrite in retaining N in compost is attributed to a pH reduction effect. The addition of other amendments like alum and zeolite to swine manure also offers a high potential for reducing NH_3 loss and increases the stability of the final compost (Bautista et al. 2011). A systematic application of these two amendments can reduce NH_3 emissions by 85–92 %, with the final compost retaining three fold more NH_4^+-N than the unamended control (Bautista et al. 2011). Furthermore, by sequestering 44 % of the retained NH_4^+-N at exchange sites, zeolite remarkably improves the quality of the compost, which acts like a slow-release fertiliser upon application to agricultural soils (Bautista et al. 2011). Thus, mineral-amended composts after application to soils improve the NUE by plants.

The application of pyrite to some problem soils (e.g. calcareous soils) can increase the availability of certain trace elements to crops, increase the nutritive parameters of forages and increase overall dry matter production. This is a very effective strategy to revegetate abandoned mine site soils. An example of the successful application of pyrite occurs in calcareous Cambisol soils in western Portugal (Castelo-Branco et al. 1999). The pyrite did not appear to pollute the surface waters or promote toxicological problems in grazing animals (Castelo-Branco et al. 1999). Thus, pyrite obtained from the ore milling industry was effective both as a soil amendment and a fertiliser for agricultural crops.

3.7 Waste Mica

Waste mica is generated during the processing of raw micas. Low-grade waste mica contains about 8–10 % K which is not readily available to plants. Most of the K in waste mica exists as structural and non-exchangeable forms. However, waste mica can effectively supply K nutrition to plants following suitable chemical and/or biological modifications. Composting has recently evolved as an efficient technology for bringing the unavailable K in waste mica into plant-available forms (water soluble and exchangeable) (Nishanth and Biswas 2008; Biswas et al. 2009; Basak and Biswas 2009, 2010; Biswas 2011). The acidic environment which prevails during composting facilitates the process (Nishanth and Biswas 2008; Biswas et al. 2009). In addition, bio-intervention of waste mica with K-solubilising bacteria (*Bacillus mucilaginosus*), N-fixing bacteria (*Azotobacter chroococcum*) and fungi (*Aspergillus awamori*) in the presence or absence of phosphate rock was effective in providing K, N and P nutrition to various crops (sudan grass, wheat and maize) (Nishanth and Biswas 2008; Basak and Biswas 2009, 2010; Singh et al. 2010).

3.8 Mineral Mixtures in Other Industrial By-Products

Several mineral-rich industrial by-products have been applied to agricultural soils in the recent years. These mainly include fly ash and red mud; the former is a by-product of coal-fired thermal power plants, whereas the latter is generated in bauxite refining factory.

3.8.1 Fly Ash

The mineralogical composition of fly ash is highly heterogeneous, depending on the raw materials (lignite, bituminous coal, etc.) and the composition and source of the coal used. Fly-ash components may include feldspars, calcite, anhydrite, quartz, calcium silicates, silica, alumina, iron oxides and high amounts of amorphous phases (Koukouzas et al. 2007; Kostakis 2009; Mishra and Das 2010). Fly ash typically contains both available and fixed forms of nutrient elements. It can be used as a more efficient source of plant nutrients than chemical fertiliser, because of the availability of nutrient elements in the former over a longer period of time (Ramesh et al. 2007; Pandey et al. 2009; Pandey and Singh 2010; Ukwattage et al. 2013). However, excessive application may cause deleterious effects including an increase in heavy-metal concentrations and the immobilisation of nutrients (Ramesh et al. 2007; Singh et al. 2008). If applied judiciously to agricultural soils, fly ash has been proven to be beneficial to crops in terms of nutrient availability and improved water retention. The beneficial effects of fly-ash application on crop productivity and nutrient uptake are improvements to soil texture and water holding capacity (WHC), reduced soil crusting and increased availability of nutrients (Srivastva and Chhonkar 2000; Gaind and Gaur 2002; Seshadri et al. 2013). A judicious application of fluidised bed combustion (FBC) ash could increase P nutrition to Indian mustard (*Brassica hirta* L.) by mineralising organic P into available P forms and immobilising inorganic P and later mobilising the bound P into available P for the second crop (Seshadri et al. 2013). A list of agricultural crops grown with fly-ash amendment in soils is given in Table 2.

Fly-ash application has distinctive effects on the soil physical properties that promote crop growth and yield. Its application to texturally variable soils (e.g. sandy clay loam, sandy and sandy loam soils) increased moisture retention at

Table 2 Application of fly ash for growing agricultural crops

Crop	Amendment	Reason for increased production	Toxicity consideration	References
Rice (*Oryza sativa* L.)	Fly ash applied to soil	Fly ash supplies plant-available silicate	Boron toxicity was avoided at a fly-ash application rate of 120 t ha^{-1}	Lee et al. (2008)
	Fly ash applied to soil	Fly ash improved physical properties of the soil, improved the germination percentage of rice seeds and improved uptake of K, P, Mn, Zn and Cu	Rice grain accumulated heavy metals below allowable limits at a fly-ash application rate of 10 t ha^{-1}	Mishra et al. (2007)
Wheat (*Triticum aestivum* L.)	Fly ash applied as foliar spray	Fly ash reduced the infestation of *Alternaria triticina* and improved the uptake of S, P, K and Ca	No adverse effect was observed at a fly-ash application rate of 5.0 g $plant^{-1}$ day^{-1}	Singh and Siddiqui (2003)
	Fly ash applied to soil	Fly ash reduced the hydraulic conductivity and improved moisture retention at field capacity and wilting point and marginally increased the uptake of micronutrients	Wheat yield increased without any adverse effects at an application rate of up to 20 t ha^{-1}	Kalra et al. (1998)
Maize (*Zea mays* L.)	Fly ash applied to soil	Fly ash reduced the hydraulic conductivity and improved moisture retention at field capacity and wilting point and marginally increased the uptake of micronutrients	Maize yield increased up to an application rate of 10 t ha^{-1} without any adverse effects	Kalra et al. (1998)
	Fly ash applied to soil	Fly ash raised the pH of acidic soils and helped to reduce the metal solubility and availability to plants	Maize yield increased without any adverse effects up to an application rate of 5 t ha^{-1}	Shende et al. (1994)
Soybean (*Glycine max* L.)	Fly ash applied to soil along with *Pseudomonas striata*	*P. striata* solubilised P from fly ash and improved P uptake by grain	A does rate of 40 t ha^{-1} did not adversely affect the inoculated bacteria and improved the yield	Gaind and Gaur (2002)
Mustard (*Brassica juncea* L.)	Fly ash applied to soil	Fly ash reduced the hydraulic conductivity and improved moisture retention at field capacity and wilting point; however, it marginally increased uptake of micronutrients	Mustard yield increased without any adverse effects up to an application rate of 10 t ha^{-1}	Kalra et al. (1998)
Palak (*Beta vulgaris* L.)	Fly ash applied to soil	Negatively impacted the palak growth and yield	An application rate of 5 % was unsuitable for leafy vegetable production; plants accumulated toxic level of heavy metals	Singh et al. (2008)
Tomato (*Lycopersicon esculentum*)	Fly ash applied to soil	Fly ash increased porosity, water holding capacity, pH, conductivity, CEC, sulphate, carbonate, bicarbonate, chloride, P, K, Ca, Mg, Mn, Cu, Zn and B uptake	An application rate of 60 % gave optimum growth without any toxic effect	Khan and Khan (1996)

field capacity, whereas the reverse trend was noted for clayey soil (Kalra et al. 2000). The moisture retention at wilting point, however, improved in all the soils with fly-ash application (Kalra et al. 2000). The incorporation of the ash in soils created significant modification in the macro- and microparticles in the soils and their pore sizes, which consequently improved the moisture retention constants (Kalra et al. 1997, 2000; Yunusa et al. 2011).

The dose at which the application of fly ash to soils is not harmful in the soil-plant systems depends largely on the soil type. For example, an application rate of up to 100 t ha^{-1} fly ash was believed to be safe for the microbial communities living in a tropical red lateritic soil (Roy and Joy 2011). The grain yield of maize and mustard increased in fly-ash-amended soils with a maximum dose of 10 t ha^{-1} (Kalra et al. 1998). The P- and S-mineralising microbial functions (e.g. phosphatase and aryl sulphatise enzyme activities) were unaffected by comparatively higher application rates of fly ash in soils (Roy and Joy 2011; Seshadri et al. 2013).

Fly ash may promote heavy-metal accumulation in soils and their increased uptake by plants (Singh et al. 2008). A number of studies have reported the immobilisation or stabilisation of heavy metals by fly ash in contaminated soils and reduced plant uptake (Dermatas and Meng 2003; Bertocchi et al. 2006). The risk of entrenching heavy metals in the food chain through the application of fly ash could be avoided if the material is used judiciously at the optimum dose, or it is used to grow nonedible economic plants (e.g. trees in the forest). A considerably greater dose of fly ash (66 % by volume) mixed with compost was reported to be a better alternative source of nutrients and a good amendment for the creation of more favourable soil conditions in dry land forests (Ramesh et al. 2007). The growth of teak (*Tectona grandis*) and leucaena (*Leucaena leucocephala*) was enhanced by an increased availability of major nutrients (e.g., P, K, Ca and Na) as supplied by fly ash which was mixed with compost (Ramesh et al. 2007). The enhanced growth of a biodiesel plant *Jatropha curcas* (measured in terms of chlorophyll content in the leaves) was reported as a result of soil amendment with fly ash at a dosage of up to 20 % (Mohan 2011).

There is evidence that fly ash promotes biological activities in soils and thereby improves plant nutrient uptake. At an application rate of up to 40 t ha^{-1}, fly ash was compatible with P-solubilising bacteria (PSB) (e.g., *Pseudomonas striata*) in a sandy loam soil and significantly improved soybean productivity by increasing P supply (Gaind and Gaur 2002). The nitrogen uptake by willow plants (*Salix* spp.) grown in a fly-ash dump was greatly improved by inoculation with *Sphingomonas* sp. which stimulated the formation of ectomycorrhizae with an autochthonous *Geopora* sp. strain (Hrynkiewicz et al. 2009). This significantly increased the shoot growth of two *Salix viminalis* clones and the root growth of a *S. viminalis* × *caprea* hybrid clone grown on fly-ash-amended soil (Hrynkiewicz et al. 2009). A greater yield of maize was achieved in soil layers overlying coal fly ash which was colonised by two arbuscular mycorrhizal fungi (*Glomus mosseae* and *Glomus versiforme*) (Bi et al. 2003). The results were attributed to the greater absorption of nutrients by the mycorrhizal plants than the non-mycorrhizal controls grown in fly-ash-amended soil (Bi et al. 2003).

3.8.2 Red Mud

India is amongst the major producers of alumina in the world and also produces approximately 4 million tons of red mud as a by-product annually (Samal et al. 2013). The mineral constituents in red mud include boehmite (AlOOH), kaolinite ($Al_2Si_2O_5(OH)_4$), quartz (SiO_2), anatase/rutile (TiO_2), diaspore (AlO(OH)), haematite (α-Fe_2O_3), calcite ($CaCO_3$), goethite (FeO(OH)), muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$) and tricalcium aluminate ($Ca_3Al_2O_6$) (Liu et al. 2011). In the recent years, red mud has received significant research attention in order to promote its use as an amendment for pollutants in solid (soils) and liquid (wastewater) phases (Bhatnagar et al. 2011; Liu et al. 2011; Feigl et al. 2012; Samal et al. 2013). It can also play a crucial role in reducing the eutrophication of rivers and waterways by retaining nutrients on infertile sandy soils (Ward and Summers 1993; McPharlin et al. 1994; Summers et al. 1996b; Snars et al. 2004). Red mud can also contribute to improved water retention in light-textured soils and can neutralise acidic soils (Ward and Summers 1993).

Like fly ash, red mud also poses a pollution risk to plants due to an extremely high pH and dispersion of soil particles due to excessive sodium. The potential harm to plants caused by a high pH value is often addressed by the incorporation of gypsum into the red mud (Summers et al. 1996a, b). A judicious application rate is required to harness the optimum effects. Red mud improved pasture production in a coarse acidic sandy soil in Western Australia when applied at rates less than 80 t ha^{-1} (Summers et al. 1996a). The improvement in production was attributed to the liming effect of the remnant alkali in red mud (present as Na_2CO_3 which is more soluble than traditional lime $CaCO_3$) (Summers et al. 1996a). The high pH value of red mud-amended soil can also be managed by biological intervention which can subsequently improve the crop yield. A phosphate-solubilising fungi *Aspergillus tubingensis* was effective in reducing the alkalinity of red mud (pH values dropped by 2–3 units) after its application to soil and improved growth and yield of maize (Krishna et al. 2005). The production of edible crops in red mud-amended soils has not obtained much interest, possibly due to the potential adverse effects of red mud. However, some success has been achieved in revegetating land that was believed to be uncultivable and barren (Chauhan and Ganguly 2011). A combination of 55 % red mud, 25 % farm yard manure (FYM), 15 % gypsum and 5 % vegetative dry dust, inoculated with bacteria and mycorrhizae, resulted in good growth of tree species (e.g. kikar (*Acacia nilotica*), karanj (*Pongamia pinnata*) and babul (*Prosopis juliflora*)) (Chauhan and Silori 2010; Chauhan and Ganguly 2011).

3.9 Other Commercial Materials

If applied to soil, a number of other mineral materials can act as a direct source of nutrients to plants. For example, granite meal is an organic fertiliser which is rich in K and contains a high concentration of silica. It greatly enhances soil structure and promotes healthier plants. Upon application, it does not alter the soil pH. Similarly, aragonite (94 % $CaCO_3$) is a rich source of calcium which is a secondary nutrient for plants. Few mineral materials can act as a source of micronutrients in soils (e.g. Azomite contains more than 67 elements beneficial to plant growth). Greensand is another organic source of K and approximately 30 trace elements. It acts as a slow-release K fertiliser. Granite powder ($<$70 μm) could also act as a slow-release K fertiliser and improved the yields of clover and ryegrass grown on acidic sandy soils over control treatment (Coroneos et al. 1995). Few siliceous volcanic rocks (e.g. perlite) and basaltic or andesitic rock (e.g. scoria) have also recently found their limited applications in gardening and landscaping activities. However, many of these minerals are expensive and not commonly used by the farmers in routine cultivation practices.

Conclusions

Mineral amendments to soils can improve the efficiency of nutrient use by plants by directly or indirectly influencing soil physical, chemical and biological parameters, which in turn control the nutrient transformation processes in soils. This amendment provides additional advantages in light-textured soils than in clayey soils, as many of the beneficial effects are due to an improvement in the physical characteristics of soils. Another direct influence can be observed where problem soils are reclaimed, by using mineral amendments. However, site-specific (precision) management technology is required to explore the beneficial effects of the mineral materials for increasing plants' NUE. The suitable application rate of various mineral amendments under heterogeneous soil and climatic conditions is also an important topic for further research. This will lead to reduced fertiliser inputs and therefore lower the cost of agricultural production. Management practices should include an integrated plant nutrition system (IPNS) for the improved utilisation of resources including mineral materials, fertilisers and organic inputs.

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