The Potential of Clay-Based Soil Ameliorants in Soil Remediation: a review

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Abstract

Current crop yields in sub-tropical countries of Africa are far below known yield potentials. Among the key drivers of declining productivity are; a reduction in the capacity of soils to retain and provide essential nutrients to the developing crop coupled with reduced water holding capacity of the soils. These have been attributed to the poor inherent physical, chemical and biological characteristics of a majority of soils found in the sub-tropics, further exacerbated by continuous cropping and poor agricultural practices. Under these conditions soil remediation is a necessity. Soil remedies such as conditioners, ameliorants and fertilizers are used to increase crop yield by making unsuitable soils capable of supporting crops that would otherwise not have been viable. Addition and incorporation of high activity clays into the soil has been shown to permanently improve soil physical and chemical properties as well as positive yield benefits. In this paper the potential of clay-based ameliorants in soil remediation and their efficacy in comparison with conventional soil amendment practices is reviewed. Such information will have significant implications in the prescription of short and long term agricultural soil quality improvement and reclamation programmes in sub-tropical regions of Africa.

Keywords: *Ameliorant, productivity, remediation, high activity clays*

1. Introduction

Sustainable agriculture in developing countries faces serious constraints due to low nutrient contents and a high rate of soil organic matter (SOM) mineralization (Glaser et al. 2002). These, coupled with the increased demand for higher crop yields, result in great pressure for cultivation of marginal lands. Cultivating marginal soils could be a promising solution in the fight against hunger especially in the developing countries. Marginal soils are however very fragile with respect to agricultural production due to their very low nutrient and organic matter content (Yanai et al. 2005). These soils are usually very acidic with high amounts of exchangeable Al and sometimes Mn (Baligar and Bennett, 1986). They are also very low in other essential nutrients like Nitrogen, Phosphorus and Potassium which are required for normal plant growth. Most marginal soils have loose structure and are highly drained with very little cation exchange capacity (Baligar and Bennett, 1986).

In an effort to boost crop production capacities large quantities of fertilizers are being added to the soil. However under tropical and sub-tropical conditions the efficiency of applied fertilizer is very low; this is related to the soils inability to retain added nutrients in an available form, this is further exacerbated by intense leaching (Baligar and Bennett, 1986). Such poor characteristics can be attributed to mineralogy. These soils have a clay fraction which is dominated by variable-charge minerals such as kaolinite and aluminium and iron oxides, which results in soils with limited capacity to retain plant-available nutrients (Bohn et al. 2001). In non-amended soils, mineralogy determines soil sensitivity, resilience and capacity to recover after exploitation (Borggaard and Elberling, 2004). Incorporation of organic and chemical amendments could improve the chemical and physical properties of these soils (Al-Omran et al. 2002).

Soil ameliorants such as manure, compost and clays have been shown to improve some soil physical properties and productivity (Miller, 1996; Mustafa et al. 1988; Choudhary et al. 1995; Falatah et al. 1996). These materials increase water supply to growing plants and improve water use efficiency (El-Hady et al. 1981; Terry and Nelson, 1986; Al-Harbi et al. 1996). They also result in an increase in organic matter content, improved nutrient status and bulk density.

Though organic ameliorants have been shown to improve soil properties and productivity (Diacono and Montemurro, 2009), their effects are not long lasting (Berthelsen et al. 2005). Organic ameliorants have been associated with accumulation of toxic elements (Diacono and Montemurro, 2009) and also infestation of fields with weed seeds, pests and pathogens. It is in light of these potential risks associated with organic ameliorants that clay amelioration is being suggested.

Managing the supply of water and nutrients to crops is probably the greatest challenge in securing world food supply without causing unacceptable environmental impacts (Powlson et al. 2011). The use of clay may improve the above mentioned constraints and thus increase soil productivity. This paper highlights the influence of clays and clay mineralogy on various soil properties and the subsequent contribution of clay based ameliorants to agricultural soil quality improvement. The efficacy of clay based soil ameliorants as compared to organic amendments is also reviewed.

2. Types of natural soil ameliorants

A soil ameliorant refers to any substance that is added to the soil to increase crop yields and to make unsuitable soils capable of supporting crops that otherwise would not have been viable (Barneveld, 2001). According to Katai et al. (2010) natural soil ameliorants can be arranged into three groups namely: green manure and other organic matter; farm yard manure and different composts; and clay-based soil ameliorants. However for the purpose of this review natural soil ameliorants are grouped into two categories; organic and clay-based ameliorants.

2.1 Organic ameliorants

Organic amelioration involves use of green manures, organic wastes such as by-products of farming, or municipal activities including animal manures, food processing wastes and municipal biosolids, wastes from some industries, such as sewage sludges, wastewaters, husks and vinasse (Diacono and Montemurro, 2009).

Soil organic matter plays an important role in long-term soil conservation and/or restoration by sustaining its fertility. It also results in sustainable agricultural production, through the improvement of physical, chemical and biological properties of soils (Sequi, 1989). The influence of organic ameliorants on soil chemical, physical and biological properties has been recently reviewed by Diacono and Montemurro (2009) and their findings corroborate with those of Sequi (1989).

Though organic ameliorants have been shown to have tremendous benefits there are a number of potential risks associated with their use. Organic ameliorants can be a source of environmental pollution, especially when they are improperly used. They can result in soil P accumulation and salinity (Miller and Miller, 2000). The use of fresh manure might result in infestation of fields with viable weed seeds, pests and pathogens. Cropland application of immature compost can produce environmental and agronomic problems. If the organic material has not been sufficiently stabilized, its application increases ammonia volatilization, decreases the soil oxygen concentration, producing some phytotoxic compounds and immobilizes soil mineral N (Diacono and Montemurro, 2009). The accumulation of toxic elements such as heavy metals in soils is often the most cited potential risk associated with organic amelioration, particularly for biosolid (Diacono and Montemurro, 2009).

Apart from the fact that clays do not pose the risks associated with organic amelioration, a number of studies have shown clays to be more effective in improving soil properties and crop productivity than organic ameliorants. Research carried out by Suzuki et al. (2007) showed that bentonite application resulted in improved soil structural stability better than compost. Baligar and Bennett, (1986) concluded that although organic matter will help in adsorption of ions, the strength of adsorption is much less than that of clay minerals. Bethelsen et al. (2005) also concluded that the addition of organic amendments such as manure or compost can be effective but short-lived in tropical environments, requiring large quantities and regular additions.

It is in light of the above mentioned potential risks and limitations associated with organic amelioration that clay ameliorants assume significance.

2.2 Clay-based soil ameliorants

The term clay is generally applied to (1) a natural material with plastic properties, (2) particles smaller than two micrometres in diameter, (3) particles composed mostly of hydrous-layer silicates of aluminum, though occasionally containing magnesium and iron (Velde and Meunier, 2008). Clay minerals are composed essentially of silica, alumina and/or magnesia, and water, but iron substitutes for aluminum and magnesium in varying degrees, and appreciable quantities of potassium, sodium, and calcium are frequently present as well (Velde and Barre, 2010).

A number of authors have reported the beneficial effects of clays. Ismail and Ozawa, (2007) reported that treating sandy soil with clay is one of the options to increase water use efficiency and productivity with the least use of mineral fertilizers. According to Harper and Gikes (1994) water repellency of sandy soil can be reduced by adding small increments of clay content. Reuter (1994) reported that clay-substrate application in sandy soil significantly improved water regime, especially on the percolation processes. Ismail and Ozawa (2007) also noted that the important consequences of clay addition are reduction of plant mineral losses and ground water contamination. Addition of clay to the top of sandy soil has been shown to be highly effective in reducing water repellency and increasing crop yield (Obst, 1989). Al-Omram et al (2005) reported that sandy soil treated with clay deposits increased the crop yield of squash (*Curcubita pepo*) by 12.8% compared with the control treatment. Clays that have shown great potential as soil conditioners include Bentonite, Vermiculite and Zeolite (Alfifi, 1986; Noble et al. 2004; Bethelsen, 2005; Suzuki et al.

2007; Mishra, et al. 2001; Jayabalakrishnan, 2007; Schundler, 2011; Sespaskhah and Yousefi, 2007; Kavoosi, 2009, Ramesh et al. 2010).

3. Influence of clays and clay mineralogy on soil properties

3.1 Influence of clays and clay mineralogy on soil structure

Soil structure development is subject to a complex interaction of many factors including soil organic matter and clay mineralogy. Soil structure is often expressed as the degree of stability of aggregates (Bronick and Lal, 2005). Aggregation results from the rearrangement, flocculation and cementation of particles. Clay minerals influence properties that affect aggregation: surface area, cation exchange capacity (CEC), charge density, dispersivity and expandibility, and these inturn affect Soil Organic Carbon (SOC) decomposition rates (Dimoyiannis et al. 1998; Schulten and Leinweber, 2000). The interaction of clay, SOC and aggregates is affected by soil pH, CEC, ions (Na^+, Ca^{2+}, Mg^{2+}), all of which are related to the type of clay minerals present in the soil (Amezketa, 1999). Low activity clays such as kaolinite and halloysites are often present in Alfisols, Ultisols and Oxisols while high-activity clays with smectites are present in Vertisols. In some soils non-crystalline clay is an important factor for aggregation, such as in volcanic soils where SOC and aggregation are associated with allophonic clay (Powers and Schlesinger, 2002). Non-crystalline clay minerals, such as allophone and imogolite, have high surface areas, and highly variable pH dependent charge properties that generally increase aggregation (Powers and Schlesinger, 2002). Non-expanding, crystalline clays, such as kaolinite (1:1), have low CEC and surface area which tend to decrease aggregate stability (Bronick and Lal, 2005). In comparison, aggregation is generally high in high-activity clays such as smectites and other 2:1 clays, which are associated with high CEC, large surface areas and high SOC (Seta and Karathanasis, 1996; Amezketa, 1999; Schulten and Leinweber, 2000; Six et al. 2000). The expandability of smectites can however disrupt aggregates during wet-dry cycles although there are variable effects possibly due to the amount of clay and number of shrink-swell cycle (Piccolo et al. 1997; Singer et al. 1992).

3.2 Influence of clays and clay mineralogy on soil biology

The differential effects of Clay minerals on microorganisms in the soil have been demonstrated (Macura and Stotzky, 1980). Clays interact with cells, viruses, enzymes, organic and inorganic nutrients and they influence the physicochemical properties of soil, the resistance of organics to microbial attack, the inactivation of toxic substances, and the activity, ecology and population dynamics of microorganisms in soil (Stotzky 1972; Filip 1973). Montmorillonite and other 2:1 clays have been shown to stimulate the respiration of bacteria (Stotzky, 1972). These effects were related primarily to the cation exchange capacity and surface area of clay minerals, among other factors, pH regulation, cation and gas exchange, and protection against hypertonic osmotic pressures (Stotzky, 1972).

3.3 Clay minerals and N fixation

Clay minerals appear to inhibit as well as to stimulate nitrification in soil (Macura and Stotzky, 1980). The inhibitory effect is manifested in soils that fix NH_4-N (e.g. Allison et al. 1951, 1953a, c; Nomik 1957; Jansson 1958; Axely and Legg, 1960; Young and McNeal 1964), probably because fixed cations are less readily exchangeable and the availability of NH_4-N to the nitrifyers is therefore reduced. The ability of clays to fix NH_4-N apparently differs; for example, high fixation by illite and vermiculite was observed under moist conditions, whereas montmorillonite fixed little or no NH_4-N (Allison et al. 1953a, b). The effect of clay minerals may result in part from their ability to sorb NH_4^+ ions, thereby reducing the level of free NH_3 (Smith, 1964), including Nitrobacter spp. (Aleem and Alexander, 1960). Furthermore, the concentration of NH_4^+ ions on external clay surfaces may enhance their availability and hence their rate of oxidation (Kai, 1968). The importance of sorption and exchange phenomen in the nitrification process has been suggested, and Lees and Quastel (1946b) indicated that only adsorbed NH_4-N is oxidized in soil. A correlation between the CEC of soils and the extent of nitrification has been observed (Lees and Quastel, 1946b; Quastel and Scholefield 1951; Smith, 1964). Macura and Stotzky (1980) also reported that the rate of nitrification was directly related to the CEC of soils.

3.4 Clays and efficient fertilizer use

The fertilizer efficiency situation in tropical farming is complex due mainly to climatic factors like high temperature and intense rains coupled with highly weathered, highly permeable soils with low cation exchange capacity (Baligar and Bennett, 1986). Soil factors have a large influence on the transformation, fixation (adsorption) and leaching losses of N, P and K which are the main constituents of fertilizers. Chief amongst these soil factors is the proportion and amounts of clay (expanding, non-expanding and amorphous material), which in turn affect organic matter content, cation exchange capacity, the concentration of ions on the exchange complex, capacity of the soil to release or renew the levels of exchangeable ion, pH, soil moisture, soil aeration and soil compaction (Allison, 1966; Barber, 1976; Munson, 1980). According to Kamprath, (1972) the largest amounts of applied phosphorus are fixed by armouphous hydrated oxides of iron and aluminium followed by gibbsite, goethite and kaolinite. Fine textured soils containing vermiculite and montmorillonite or smectite clays will have more potassium than soils predominant in kaolinitic types of minerals, which are more weathered and low in potassium. Soils with a large proportion of vermiculite fix considerable amounts of K (Baligar and Bennett, 1986).

4. Bentonite, vermiculite and zeolite as soil ameliorants

4.1 Bentonites as soil ameliorants

Bentonites are highly colloidal and plastic clays composed mainly of montmorillonite and are formed by the alteration of volcanic ash in situ (Grim 1953). Its high sorption capacity, swelling ability, large active surface properties play the most important role in agricultural applications (Mishra et al. 2001). Sallam et al, (1995) concluded that mixing shale deposits (comprising 72% clay and having smectite as the dominant mineral) with sand at different rates improved the physicochemical properties, and in particular the soil moisture characteristics and cation exchange capacity. Abou-Gabal, et al. (1990) found that the addition of local Tafla (dominantly bentonite) to sandy soils in Egypt improved the soil texture and consequently soil-water plant relationships. El- Sherif and El-Hady (1986) revealed that mixing local bentonite with sandy soil improved its mechanical, hydrophysical and chemical properties and consequently increased water use efficiency.

Afifi (1986) also reported that the addition of bentonite to sandy soils increased the retention and availability of soil moisture as well as the increase of the cohesive forces among their particles. Das and Dakshinamuri (1975) showed that the infiltration rate and hydraulic conductivity of sandy loam soils treated with bentonite were reduced compared to untreated soils. They concluded that horizontal infiltration as well as the diffusity was very much reduced in the treated soils.

Singh (1982) reported that, in the arid zone of Rajasthan, India, application of bentonite at the rate of 40t ha^{-1} in sandy soil in the surface 20cm increased the moisture storage at 10 KPa from 12% to 17%. He further documented the reduction of moisture losses through deep percolation by incorporation of bentonite as a subsurface barrier for better tree establishment.

In studies carried out in Northeast Thailand by Suzuki et al. (2007), it was shown that application of bentonite enhanced porosity and altered pore size distribution resulting in an increase in the available water content for crop growth. In a separate experiment, in a glasshouse pot trial, Bethelsen, 2005 reported that water retention curves demonstrated a significant increase in plant available water (PAW) with increasing rates of bentonite. Additions of bentonite equivalent to 0, 25, 50, and 75 t ha^{-1} provided PAW contents of 0.085, 0.086, 0.090, 0.117 g cm^{-3} (equating to a change in gravimetric water content of 5.5, 5.6, 5.9 and 7.6% respectively at the soil bulk density of 1.53 g cm^{-3}). This increased PAW due to bentonite application was also associated with taller plants with thicker stems (Bethelsen, 2005).

In a laboratory study carried out in India Mishra et al. (2001) concluded that physical, chemical and hydraulic properties of a native alfisol were changed remarkably with the addition of bentonite. They also concluded that the plastic and flow limits, volume, dispersion ratio, pH and CEC increased with the addition of bentonite to the alfisol.
When bentonite is added to the soil, the mineral nutrient and colloid content of soil increases and with higher colloid content, the leaching of different nutrients decreases (Noble et al. 2000). The addition of bentonite clay to degraded sandy soils has clearly demonstrated the potential role of clay ameliorants in restoring the reproductive capacity of soils within a single season (Berthelsen et al. 2005). Studies carried out by Noble et al. (2004) over a three year period showed that responses from this form of intervention are persistent and continue to increase.

4.2 Vermiculite as a soil ameliorant

Another high activity clay that has proven its worth as a soil ameliorant is vermiculite. Vermiculite is the geological name given to a group of hydrated laminar minerals that are magnesium-aluminium-iron silicates with a suggested formula of $(Mg, Fe^{2+}, Al)_3(Al,Si)_4O_{10}(OH)_2\ 4H_2O$ (Harben and Kuzvcort, 1996). Interlayer ion exchange and the lattice replacement of Al for Si in its tetrahedral sheets and Al and/or Fe for Mg in the octahedral layers are among the factors that give vermiculite a large number of exchange sites and high exchange capacity (Abollino et al. 2007; Fitzpatrick, 1983; Grim, 1953). Pure vermiculite has a high CEC of more than 110 meq/100g (Walker, 1961). Vermiculite is mostly used after heating in order to get a porous less dense material. The purpose of heating vermiculite is to get products with the ability to retain plant available water and a favourable pH for their growth (Marwa et al. 2009).

Jayabalakrishnan, (2007) reported that vermiculite application at 5 tonnes ha^{-1} resulted in the yield increases of sunflower grain and stalk which was nearly 1.68 and 1.41 folds increase respectively over the control. Such yield increases were attributed to the effect of vermiculite which enhanced the CEC and physical environment of the soil resulting in possible increase in the productivity of the crop. In the same experiment Jayabalakrishnan, (2007) also noted that in a treatment that received a high rate of vermiculite (10t ha^{-1}), grain and stalk yield of sunflower was just 1.08 and 1.03 % increase respectively over the control. This he attributed to high pH (8.51) and EC (073 dS m^{-1}) due to a high rate of vermiculite application. He also suggested high nutrient adsorption on vermiculite adsorption sites resulting plant nutrients being unavailable as another reason for the reduced productivity.

In Brazil it was discovered that incorporating a small amount (1 cubic meter per hectare) of vermiculite at the bottom of furrows resulted in increased water retention by soils (Schundler, 2011). Application of vermiculite at the bottom of furrows below the level of fertilizers was also shown to reduce leaching when heavy precipitation (150mm in a single day) occur and therefore reduce loss of fertilizer. In the same study Vermiculite incorporation was shown to increase soyabean yield by 56 %, 15 % in corn and 30 % in coffee (Schundler, 2011).

4.3 Zeolite in soil quality improvement

Zeolites are crystalline aluminosiliocates, with a general formula $M_xD_y[Al_{(x+2y)}+2_ySi_{n-(x+2y)}O_{2n}]mH_2O$, where x is the number of monovalent cations, y the number of bivalent cations, n the cation valence and m the number of water molecules in the formula (Ramesh et al. 2010). They are tectosilicates exhibiting an open three-dimensional structure containing cations needed to balance the electrostatic charge of the framework of silica and alumina tetrahedral and containing water (Hemingway and Robie, 1984). Their two most important minerals are Clinoptile and Mordinite tectosilicates (Matyas, 1979).

Natural compounds such as Zeolite (Z) minerals have been reported as ameliorants to decrease N leaching (Huang and Petrovic, 1994; Chimic and Torma, 1992), and to increase N recovery. Clinoptile (a natural Z) due to its large CEC is a potential carrier for plant nutrients including NH_4^+, to be released slowly for continuous uptake by plants (Sepaskhah and Yousefi, 2007). According to Eberl (2002), application of a mixture of Z and urea fertilizer to soil resulted in less nitrate leaching by decreasing the nitrification process through ammonium adsorption on Z. Because of its high exchange capacity, clinoptile has often been used as an inexpensive cation exchanger to control ammonium (NH_4^+) release (Allen et al. 1993, 1996). Natural Zeolite has also been used for remediating heavy metal polluted soils (Shi et al. 2009). Furthermore, zeolite can retain soil water because of its high specific surface area (Shi et al. 2009). Pepper et al. (1982) applied clinoptile type of Z at a rate of 8% to a sandy soil and indicated a decrease in NO_3^- and NH_4^+ leaching and an increase in the N-use efficiency of turf grass. Application of 8 t ha^{-1} of Z along with 60 kg ha^{-1} of N as urea in a light textured soil where water was high increased the rice yield (Kavoosi, 2009).

Zeolites have been reported to improve soil physical properties. They may hold more water than half of their weight due to high porosity of the crystalline structure (Ramesh et al, 2010). Water molecules in the pores could easily be evaporated or reabsorbed without damage to such structures. In a study carried out by Voroney, (1988), amendment of sand with zeolites was shown to increase plant available water by 50 %.

In a plant growing experiment in which zeolite was used as nutrient supply, it was shown to decrease acidity, favourably influencing micro-element supply (Ghrair et al. 2008) moreover it also promoted water lifting of plants and improved soil water management (Pepper et al. 1982).

Zeolitic amendment is an effective way to improve soil condition in an arid and semi-arid environment (Yasuda et al. 1998). Zeolites have been tested for use as a soil amendment on various crops, including vegetables and in greenhouses in Russia, field crops in Japan, as constituents of golf course greens in order to improve compaction resistance, and reduce leaching of pesticides and fertilizers from the soil (Wallace, 1998).

Succinctly, clay ameliorants have been shown to alter the fundamental processes that influence erosion, e.g. increase pore space in soils, increase infiltration, enhance soil aggregation, reduce soil sealing, reduce soil crusting, decrease wind erosion, reduce rain splash detachment, and reduce soil erosion by concentrated overland flow (Martin, 1953; Chepil, 1954; Wallace and Nelson, 1986; Fox and Bryan, 1992; Sojka and Lentz, 1994; Nadler et al. 1996): improve soil moisture balance, improved nutrient storage and the create of an environment more conducive to biomass production (Sutherland and Ziegler, 1998).

5. Potential challenges to widespread adoption of clay ameliorants

Though clay based soil ameliorants show immense potential in alleviating soil production constraints, there are challenges that are likely to hinder their widespread adoption. One of the challenges will be the availability of high activity clays locally. However considering the benefits that will accrue from savings on fertilizer costs and improved production, it will still be cost effective to import these from areas or countries where they are mined.

Selection of the appropriate type of clay ameliorant and the rate at which it should be applied for maximum productivity in different soils is also likely to be a serious challenge. To tackle this challenge there is need for coordinated research in all countries facing soil degradation and soil infertility problems, so as to identify the appropriate ameliorants for particular soils and to subsequently come with the appropriate application rates.

6. Conclusion

The use of high activity clay based soil ameliorants in soil remediation shows immense potential especially considering that clay amelioration does not pose the risks associated with organic amelioration. In areas where natural deposits of these high activity clays are abundant, soil amelioration using clay based amendments is a cheap and permanent way to improve soil quality for crop production. When compared to the cheapest conventional natural source of soil amendments, which is organic matter, clay based ameliorants have been shown to improve soil physico-chemical better than some organic amendments and the positive effects of clay remediation are more durable as compared to that of organic amendments. However it is important to note that an interaction of these soil amendment groups is likely to result in better results as compared to their individual effects.

Further research should however be carried out to determine suitable clay ameliorants for different marginal soils in different parts of the world and also the appropriate application rates, so as to improve the soils physical, chemical and biological properties to create optimal conditions for crop growth without adversely affecting the environment. Further research on the interaction of organic and clay based amendments when used in soil remediation will also shed more light on the possible use of these in combination.

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