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Influence of Clay Minerals on Some Soil Fertility Attributes: A Review

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Abstract

Clay minerals constitute an important component of the soil system and knowledge of their role in soil fertility is imperative for sustainable soil management and productivity. The aim of this work is to overview the influence of clay minerals on some major soil fertility attributes. The rationale for carrying out this work is that most soil fertility studies rarely incorporate soil mineralogy. Clay minerals, through their physical and chemical properties, affect soil fertility by controlling nutrient supplies and availability, through the sequestration and stabilization of soil organic matter, by controlling soil physical properties through microaggregate formation, by influencing soil acidity and controlling soil microbial population and activity. The main processes involved in these relationships are dissolution-precipitation and adsorption-desorption processes, alongside mechanisms involving the formation of short-range-ordered phases. Although the determination of soil mineralogical properties is very costly and time-consuming, information about a soil's mineralogy is imperative for a holistic understanding and proper management of soil fertility. Therefore, the development of rapid, low-cost, reliable and efficient techniques of soil mineralogical analysis, directly applicable to soil fertility investigations, constitutes a major challenge. Also, future research should investigate the relationships between clay minerals and soil nitrogen vis-à-vis sequestration and stabilization. Lastly, clay minerals should be considered in studies dealing with soil quality assessment, especially in the choice of soil quality indicators.

Keywords

Clay Mineralogy, Nutrient Supply, Ion Adsorption-Desorption, Mineral Dissolution-Precipitation, Nutrient Availability

1. Introduction

Soil fertility is defined as "the quality of a soil that enables it to provide nutrients in adequate amounts and in proper balance for the growth of specific plants or crops" [1]. Soil fertility combines several soil properties including chemical, physical, biological and mineralogical, all of which affect directly or indirectly nutrient dynamics and availability [2]. Soil mineralogical properties appear to have a significant role in soil fertility management [3] but seem to be ignored in most studies, even in fertilizer recommendations [4], especially in Africa [5].

Clay minerals are naturally inorganic compounds with definite physical, chemical and crystalline properties and are classified as primary or secondary, silicates or non-silicates and crystalline or amorphous [6]. Primary minerals form at elevated temperatures and pressures, and are usually derived from igneous or metamorphic rocks, while secondary minerals are the culmination of either alteration of the primary mineral structure or neoformation through precipitation or recrystallization of dissolved constituents into a more stable structure [7] [8]. Common primary minerals in soil environments include silicates, oxides of Fe and Al, Zr and Ti, and phosphates, while typical secondary minerals found in soil environments include alumino-silicates, oxides and hydroxides, carbonates, sulphates and amorphous minerals [6]. Secondary minerals are mainly found in the clay-sized and fine-silt-sized fractions, and form the most reactive inorganic materials in soils [9], thereby influencing availability of nutrient elements through various mechanisms. Soil clay minerals are grouped into 1:1 and 2:1 clay minerals, depending on the ratio of silica tetrahedral sheet to alumina octahedral sheet. The 1:1 clay minerals, primarily kaolinite, are found in most soils, but predominate in highly weathered soils of humid tropical regions. In tropical environments, sesquioxide minerals rich in Fe and Al dominate. The 2:1 swelling or expandable clays include the smectite and vermiculite groups, which have large surface areas and high cation exchange capacities (CEC). These clay minerals play a significant role in dictating the suitability and behaviour of soil for various land uses. Clay mineralogy-soil fertility relationship is an imperative component in understanding and managing soil fertility for sustaining crop production, especially in the tropics [10] [11].

Clay mineralogy appears to be one of the most important indicators of soil quality [12], and proper knowledge of the clay mineralogy of a soil has significant practical implications on the use of fertilizers, on application and management [13] [14] [15] [16], and on the bioavailability of heavy metals in soil [17]. Furthermore, soil mineralogy-soil fertility relationship is a basic component in understanding and interpreting the results of fertility experiments and soil analytical data, especially in developing fertilizer recommendation systems [18] [19] [20]. Unfortunately, many soil fertility studies have hardly considered the role of soil mineralogy in understanding soil fertility and nutrient dynamics in agro ecosystems [21]. The lack of integrated soil mineralogy-soil fertility studies is indicated by the lack of interest by soil fertility researchers in carrying out detailed

soil mineralogical studies [22] and also the tedious processes involved in characterization, identification and quantification of clay minerals. Another reason is the lack of inexpensive and rapid spectroscopic techniques for soil characterization, especially in developing countries [23]. Notwithstanding, a holistic understanding of soil fertility management must incorporate soil mineralogy since it has often been inferred that knowledge of the properties of these reactive materials should enable close predictions of the useful soil properties, whether for growing plants, or for other purposes [9]. According to Karathanasis [24], the effect of the soil mineralogical composition on soil productivity is two-fold; 1) it influences chemical reactions regulating nutrient availability and uptake and 2) it affects physical properties controlling soil moisture balance and physical conditions of the soil. In order to make visible the link that exists between clay minerals and soil fertility, a summary is presented on the influence of clay minerals on nutrient supply and availability, the role of clay minerals on soil organic matter retention, the relationship between soil mineralogy and soil physical properties, the relationship between soil mineralogy and soil acidification, and the influence of clay minerals on soil microbial activity.

In this review, we consider two important properties of clay minerals capable of influencing soil fertility. The chemical property considered is the cation exchange capacity and the physical property considered is the surface area. We focus on the direct influence of the physicochemical properties of clay minerals on the physical, chemical and biological properties of soil and also on the direct and indirect influence of clay minerals on nutrient availability. Due to the large number of publications relating soil mineralogy and different soil properties, we cannot give an exhaustive overview of all the works—rather, we focus on the most relevant ones that directly relate to soil fertility and plant growth, thereby making a synthesis of both earlier studies and recent ones.

2. Role of Clay Minerals in the Supply and Availability of Plant Nutrients

Of the three major soil components (solid, liquid and gas), the solid fraction is constituted by soil minerals and organic matter, which exert significant direct and indirect influences on the supply and availability of most nutrient elements [25] [26] [27]. The main processes involved in the release and fixation of nutrient elements in soils include dissolution-precipitation and adsorption-desorption. Soil minerals therefore act both as sources and sinks of essential plant nutrients. Of the seventeen elements considered as being essential for plants, most (N, P, K, Ca, Mg, S, B, Cl, Mn, Fe, Zn, Cu, Mo and Ni) are derived from the soil solution while few others are derived from water (O and H) and air (N, C, O) [28]. Through the weathering of primary minerals, plant nutrients are released into the soil solution. These weatherable primary minerals act as an important reservoir for these elements. Micas and illite are the most important sources of K in many soils [29] and they also contain Mg, Fe, Ca, Na, Si, and a number of micronutrients. Significant amounts of Ca, Si and smaller amounts of

Cu and Mn are present in feldspars. Amphiboles and pyroxenes are vital reservoirs of Mg, Fe, Ca, Si, and most of the micronutrients. Although the weathering rates of primary minerals for certain elements may not be fast enough to meet plant nutrient requirements on a short-term basis, particularly in managed cropping systems, mineral weathering is an important and long-term source of several geochemically derived nutrients [6].

Generally, the available nutrient supply in soils is considered to be the sum of both soluble and exchangeable forms. The capacity of the soil to replenish the solution nutrient concentration after it has been lowered, e.g. by plant nutrient uptake, leaching, fixation, depends on the mineralogical composition of the soil. This is because a great portion of the cation exchange capacity of the soil, which determines the ability of the soil to supply growing plants with nutrients, is related to crystalline and amorphous mineral components. The magnitude of the ion exchange reaction is determined by the type of ions involved, nature of the soil solution and the strength of attraction between a particular mineral and a specific cation [24]. Adsorption reactions involving minerals are often more important in controlling plant nutrient element availability than the release of nutrient elements by mineral weathering. Phyllosilicates with a permanent charge (e.g. vermiculite and smectite) offer exchange sites that hold a number of essential nutrients in their cationic form (cation exchange capacity), such as Ca²⁺, Mg²⁺, K⁺, and Na⁺ [30]. The nutrients are retained by outer-sphere complex formation and may be taken up by plant roots through diffusion and mass-flow transfer processes [31] [32]. On the other hand, variable charge minerals with low CEC/AEC and low crystallinity (e.g. Fe oxides) often have higher affinity for anions (e.g, H₂PO₄, NO₃), especially under acid pH conditions [33] [34].

Figure 1 summarizes the role of clay minerals in the release and availability of soil nutrients. As indicated in the figure, not all the added nutrients from fertilizers, for example, will be available for the plants. Apart from the well-known losses through leaching and volatilization, clay minerals can readily adsorb the added nutrients from fertilizers and render them stable and non-exchangeable. Thus, knowledge of the type and quantity of clay minerals is important for fertilizer application and use efficiency. However, the adsorbed nutrients can become available if appropriate management (e.g. soil pH amelioration) is carried out so as to create a conducive environment that can enhance nutrient desorption.

Figure 1 further shows that clay minerals control nutrient availability through the influence of physical, chemical and biological processes involved in nutrient release and cycling (desorption, dissolution, mineralization, adsorption, precipitation, and immobilization). There is also an intrinsic link between clay minerals and the labile and non-labile nutrient pools.

2.1. Role of Clay Minerals on Nitrogen, Phosphorus and Potassium Availability

In general, the bulk of plant available nitrogen in soil comes from mineralization

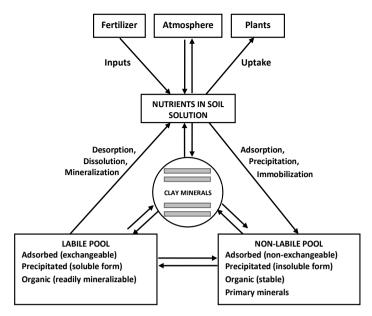


Figure 1. Role of clay minerals on nutrient supply and availability. Source: Adapted from Delgado and Gomez [35].

of soil organic matter [36]. There is also a large amount of soil nitrogen that derives from the weathering of nitrogen-bearing parent materials such as mica-schists [37] and nitrogen-rich siliciclastic rocks [38] [39] [40] [41] [42]. Nitrogen from the soil solution is usually taken up by plants in the form of nitrate (NO₂) and exchangeable ammonium (NH₄) ions. In soils dominated by variable surface charge minerals (kaolinite and Fe and Al oxides) such as Oxisols and Ultisols, the capacity to retain large amounts of NO₂ N, particularly in the subsoil horizons is evident. For example, Lehmann et al. [43] observed 150 - 300 kg·ha⁻¹ NO₃ N in a Brazilian Oxisol up to a depth of about 2 m. Rasiah and Armour [44] equally estimated between 17 - 32 t·ha⁻¹ NO₃ N to a depth of 10 m under different land uses in Oxisols from northern Queensland in Australia. The large adsorption of NO₃-N was due to the high anion exchange capacity (AEC) of the soils. Under laboratory conditions using batch experiments, Kothawala and Moore [45] observed that different forest soils (including Podzols, Brunisols, Luvisols, Gleysols, and an organic soil) from Canada showed different degrees of dissolved nitrogen adsorption (NH₄ and NO₃) due to differences in their mineralogical compositions. The adsorbed nitrogen in soil by clay minerals is a major contributing factor to soil N depletion and loses, especially in subsoil horizons where the type of minerals favour their retention [43] [46]. Many studies have also reported the presence of nitrogen in various bed rock types ranging from 0.1 - 1050 mg·Kg⁻¹ N in igneous and granitic rocks and >1000 mg·Kg⁻¹ N in some sedimentary rocks [47]. Thus, such adsorbed nitrate is likely inaccessible to most field crops because it is found at great depths. Fixation and defixation of NH₄ in soil is highly dependent on clay mineral composition [14] [47] [48]. In contrast to highly weathered oxisols and ultisols with variable charge minerals, soils with permanent charge minerals and high cation exchange capacity (e.g, smectite, vermiculite, illite and interstratified minerals with 2:1 layers) have the ability to retain ammonium (NH⁴₄) ions. A large proportion of the NH₄ Nitrogen is retained in the interlayers of 2:1 phyllosilicates and is not readily exchangeable [49]. The process of NH₄ fixation is similar to that of K+ fixation due to similarity in ionic sizes and valence properties, and therefore competes for the same non-exchangeable sites of 2:1 clay minerals [47] [48]. Thus, the presence of K⁺ in soil (from K-bearing minerals) greatly influences plant nitrogen (in the form of NH₄) availability especially when it is applied in the form of ammonium N-fertilizers such as ammonium sulphate ((NH₄)₂SO₄) and ammonium nitrate (NH₄NO₃) [14]. Therefore, field experiments aimed at investigating crop response to N-bearing fertilizers necessitate complementary soil mineralogical investigations for a better interpretation of experimental results. With the exception of sandy soils, the amount of fixed NH₄ in the soil ranges from about 350 - 3800 kg·ha⁻¹ NH₄ -N in the top 30 cm of soil; vermiculite and partially weathered illite generally have a greater capacity to fix NH₄ in soils than the smectite group of minerals [48] [50]. The behavior and capacity of 2:1 phyllosilicates in fixing NH₄⁺ ions is related to the magnitude and origin of negative charge in these minerals. NH⁴ -fixation generally increases with the increasing amount of layer charge in the 2:1 phyllosilicates. In earlier studies, Sahrawat [51] observed that NH₄ fixing capacity of 12 tropical rice soils was neither related to soil pH, SOM nor clay content but rather to the amount of active iron in the soils due to the reversible redox behavior of iron oxides in the soils. Equally, Gouveia and Eudoxi [52] found that NH₄ fixation was significantly related to soil type (where soils with illitic minerals showed the highest fixation) but contrary to the observations of Sahrawat [51], the fixed amount of NH₄ was related to clay content, soil pH and SOM.

Phosphorus is primarily taken up by plants in the form of orthophosphates (either as HPO₄²⁻ or HPO₄⁻) depending on the pH of the soil medium [53] [54]. The concentration of P in soil water is generally very low (<0.01% of the total soil P), with the bulk of the soil P existing as organic P, insoluble compounds of P with Al, Fe, and Ca, and phosphate adsorbed to Fe and Al oxides and phyllosilicates [50]. Generally, the sorption of phosphates is affected by the type and nature of the reactive sites of clay minerals. Oxides and hydroxides of Fe and Al such as hematite, goethite and gibbsite are species primarily responsible for the adsorption of large quantities of phosphates [54] [55]. The availability of phosphate ions for plant uptake is greatly dependent on reactions with clay minerals through adsorption and precipitation processes [54]. In the specific case of volcanic soils, alumino-silicate minerals such as allophane, imogolite and Fe- and Al-oxides retain huge quantities of soil organic phosphorus [56] through various mechanisms involving association with humic substances and expandable phyllosilicates [56] [57]. According to Stutter et al. [58], the phosphorus retained in the lattices of these minerals is protected from microbial and enzymatic decomposition, making it deficient for plant uptake. However, other studies have shown that microorganisms are capable of converting soil P (fixed) to

plant-available orthophosphate through a three-step process [59] These processes are: 1) P bound in mineral and organic matter complexes is solubilized by plant or microbial organic anions and acids, 2) solubilized organic P is mineralized by phosphatases to release orthophosphate, and 3) both solubilization and mineralization processes occur proximal to the plant root.

The most important potassium-bearing minerals in soils are alkali feldspars (20 to 30 g·kg⁻¹ K), muscovite (K mica, 60 to 90 g·kg⁻¹ K), biotite (Mg mica, 36 to 80 g·kg⁻¹ K), and illite (32 to 56 g·kg⁻¹ K) [32] [60] [61] and total soil K concentration typically ranges from 0.2% to 3.3% of the total soil mass [32] [61]. These are the main natural potassium sources from which K⁺ is released by weathering. In natural soils, potassium is derived ultimately from the potassium silicate minerals with over 90% - 95% of K existing in the structure of these minerals [13] [32] [62]. In deeply weathered, highly oxidized soils that have low organic matter, it is essentially the clay minerals that are responsible for the release of exchangeable K that is measured in soil analysis [19] [29] [63]. Under these humid conditions, soils become acidic, thereby promoting the formation of chlorite from K+-selective 2:1 minerals. Thus, soils developed under humid conditions have a poor K⁺-selective binding capacity and are low in potassium [60]. During the alteration of micas (biotite and muscovite), K+ is replaced by hydrated cations such as Mg²⁺ or Ca²⁺, thus rendering it available for plants [9]. A combination of soil mineralogy, physicochemical properties and soil moisture regime gives a better insight into the effects of clay minerals on different forms of K in soil [64] [65] [66]. Raheb and Heidari [65] observed that non-exchangeable potassium in smectite—dominant soils was lower than those dominated by vermiculite, hydroxy-interlayered vermiculite and illite, and there were significant correlations between exchangeable potassium and clay content, organic carbon and cation exchange capacity. Similarly, Bajwa [64] observed that beidelitic clays can fix > 80% of K under aquic soil conditions. In another study to investigate the kinetics of non-exchangeable K release as a function of soil mineralogy and soil type, it was observed that the rate of K release was greater in soils dominated by expansible clay minerals, notably smectites and vermiculite, compared to soils dominated by chlorite, palygorskite and illite [67]. In addition to type of clay mineral, it has been reported that K fixation capacity of calcareous soils correlated strongly with clay content and CEC [68]. Thus, it is very important to evaluate the effects of vermiculitic and illitic soils on the application of NH₄ and K⁺-based fertilizers and nutrient use efficiency of crops. A recent investigation showed that the uptake of K by plants was as a function of the amount of K released from the clay mineral, and the amount of K released or adsorbed (in the case of fertilization) was highly dependent on the mineralogical composition of the clay mineral [66].

2.2. Role of Clay Minerals on Availability of Micronutrients (B, Cl, Mn, Fe, Zn, Cu, Mo, Ni)

Among the micronutrients needed by plants, Fe, Mn, Cu, Zn, and Ni are taken

up in their cationic forms, while B, Mo, and Cl are taken up in their anionic forms. Copper is most abundant in mafic (rich in Mg, Ca, Na, and Fe, commonly basalt and gabbro) rocks, with concentrations ranging from 60 to 120 mg·kg⁻¹ Cu. High Zn concentrations (about 95 - 100 mg·g⁻¹ K) are derived from basaltic igneous rocks and shale; one of the five major pools of zinc in soil is primary minerals and secondary alumino-silicate materials [69]. In soils, iron is mainly present in the insoluble Fe³⁺ form, but other forms exist depending on the pH and moisture conditions of the soil. It occurs as Fe (III) oxides and constitutes the major components of some highly weathered mineral soils (Oxisols) with very low CEC. Nickel is primarily derived from soils developed on basic igneous rocks with concentrations ranging from 2000 to 6000 mg·kg⁻¹ Ni [70].

Most of the available boron in soil is believed to be derived from marine sediments as evaporates by chemical precipitation and include borax, colemanite, ulexite, inyoite, and inderite [71]. These boron minerals are made up of hydrated calcium, magnesium, and sodium boron minerals. In most of the well-drained soils formed from acid rocks and metamorphic sediments, the most common boron-containing mineral is tourmaline [71] [72]. In neutral or acidic soils, the dominant boron form is the neutral molecule B(OH)3 (boric acid), while in alkaline soils, significant amounts of boron occur in the form of the borate anions (either $B(OH)_4^-$ or BO_3^{3-}) [71]. Considering the neutral molecule $B(OH)_3$, boron stands as the only essential element taken up by plants in the form of a neutral (uncharged) molecule. Soil texture has been reported to affect B availability in soils, owing to the clay minerals present in soil. Gupta [72] observed that B deficiency is higher in coarse-textured soils than in fine-textured soils due to the high leaching of boron in sandy soils. Since boron has a coordination number of four, soils rich in phyllosilicate minerals such as phlogopite, saponite, illite and montmorillonite, harbour boron in their lattices where they substitute for tetrahedral silicon and aluminium [71].

Soil parent materials with the highest concentrations of molybdenum include phosphorite, shale, limestone, and sandstone [73], and the available molybdenum content generally increases with increase in alkalinity or fineness of the soil texture [74]. Mineral forms of molybdenum commonly present in soils include molybdenite (MoS₂), powellite (CaMoO₄), wulfenite (PbMoO₄), ferrimolybdite (Fe₂(MoO₄)), ilsemanite (molybdenum oxysulfate), and jordisite (amorphous molybdenum disulphide) [73] [75]. Under low pH conditions, Mo is readily adsorbed in soil by Fe and Al oxides, kaolinite, illite and montmorillonite [76].

Manganese is most abundant in soils developed from rocks rich in iron owing to its association with this element. Adsorption reactions play little role in controlling the availability of Fe and Mn in soils. Rather, oxidation and precipitation reactions predominantly control the soil solution concentration of Fe and Mn [77] [78]. Goethite, hematite, and ferrihydrite are the most commonly occurring secondary Fe oxides in soils. Due to the microcrystalline size of Fe oxides, these minerals possess high specific surface areas and provide numerous adsorption

sites for both cationic and anionic elements in almost all soil types. The two most stable Fe oxides, goethite and hematite, are known to have substantial structural substitution of trace elements, including Mn, Ni, Zn, and Cu [79]. Kumar and Babel [80] observed that availability of Cu and Zn increased significantly (p < 0.05) with increase in finer soil fractions (silt and clay) but decreased in soils having high $CaCO_3$ contents. This observation can be explained by the increased solubility of Cu and Zn under acidic conditions (pH < 5.5) compared to alkaline conditions (pH > 7). The increased solubility of these elements may lead to toxicity.

Copper in soil is present as sulfide minerals, stable oxides, silicates, sulphates and carbonates [81]. The most abundant copper-containing mineral is charcopyrite (CuFeS₂). The concentration of copper ions in soils varies from 6 to 60 mg·Kg⁻¹ [82]. The availability of copper in soil is controlled by reduction-oxidation conditions which can be affected by many factors such as water logging and compaction [78]. Additionally, increased solubility of Cu is favoured by acidic conditions (pH < 5.5), which might lead to toxicity. Generally, adsorption and desorption of Cu2+ in soils is affected by the proportion of variable-charge and permanent-charge minerals in soils [83] and also by the nature (type) of the soil mineral [84] [85] [86]. On the other hand, Zinc is associated with hydrous oxides and carbonates through adsorption, surface complex formations, ion exchange, incorporation into the crystal lattice, and co-precipitation [69]. Fe and Mn oxides are common mineral constituents in many soils and are important substrates for the retention of many macronutrients and micronutrients. Cu, Zn, and Ni are adsorbed by Fe and Al oxides by forming complexes at low solution concentrations. Generally, the adsorption of Cu²⁺, Zn²⁺, and Ni²⁺ occurs by complex formation on negatively charged surfaces of 2:1 phyllosilicates and through complex formation on kaolinite surfaces [79].

Boron and Mo are taken up by plants as H_3BO_3 and MoO_4^{2-} respectively. In a similar manner to Zn, Cu and Ni retention, MoO_4^{2-} is strongly adsorbed by metal oxides. Chlorine is taken up by plants in the chloride (Cl⁻) form, and adsorption reactions involving Cl⁻ ions are similar to those involving NO_3^- ions. Chloride is not adsorbed by minerals at pH levels above 7.0 and is only weakly adsorbed in kaolinitic and oxidic soils that have positive charges under acid conditions [79].

3. Role of Clay Minerals on Soil Organic Matter Retention and Stabilization

Soil organic matter (SOM) is both a source and a sink of plant nutrients [87]; it is an ion exchange material; it promotes the formation of soil aggregates and thus influences soil physical properties and soil moisture; and it is an energy substrate for soil microbes and macrofauna [88] [89]. Approximately 80% of the organic carbon (OC) that is active in the terrestrial carbon cycle is stored in soils [90] [91]. The bulk of nitrogen-containing organic matter appears to be bonded

chemically to clay minerals and protected physically in soil aggregates rather than existing as complex chemical molecules of plant and microbial residues [92]. This sequestration is achieved through various mechanisms which include the formation of clay-humic complexes, sorption of organic matter on clay particles, fixation of organic carbon in the crystal lattices of clays and the formation of organo-metallic compounds such as Ca, Fe and Al humates through humification processes [93] [94] [95] [96]. These complexation and humification processes lead to the overall stabilization of SOM by clay minerals [95] [97] [98]. In the particular case of arable soils, SOM is primarily stored in fine-particle-size fractions [99] [100] [101] and stable SOM constituents are primarily related to the proportion and characteristics of these fine particles in soils [102]. However, the type and quantity of clay minerals in these soils play an important role in retaining the added organic C and N in soil [103] [104]. In this case, the SOM is retained through physicochemical stabilization and aggregate formation [105]-[110].

Generally, phyllosilicates such as smectites are more intimately associated with retaining and increasing SOM than the other clay minerals [91] [111] [112], mainly due to their high specific surface area and CEC [113], even though contrary observations have been reported [114] [115] [116]. Some other studies have shown that Fe and/or Al oxides can also have a large influence on the retention of OC in soil and usually are better adsorbents for OC than phyllosilicates [112] [117] [118]. This observation has been attributed to the abundance and hence the overall increase in surface area of these oxides [108] [117]. This observation is usually common in high altitude Oxisols where the rate of organic matter mineralization is reduced, due to lower temperatures. Allison [88] observed that under similar climatic conditions, OC contents in fine-textured (clayey) soils is about 2 to 4 times greater than in sandy soils, due to lower surface area in the latter, as well as higher mineralization associated to increased aeration. In contrast, Yerima and Van Ranst [119] reported that some coarse-textured soils such as andisols store huge quantities of OM than some fine-textured soils due to the formation of allophane-organic matter complexes inherent in such soils, an observation similar to that reported by Singh et al. [120].

Notwithstanding, this debate has been clarified by other studies. For example, Wagai and Mayer [121] observed strong correlations between iron oxides (Fe_x. O_y) and organic matter in a wide variety of soils spanning 8 different orders from different parts of the world and concluded that high volumetric ratios of organic matter to Fe_xO_y are due to organic matter stabilization through mechanisms involving organo-Fe complex formation or tertiary associations among Fe_xO_y , OM and other soil minerals, and not through the commonly reported sorption mechanisms found in the literature. Similarly, Singh *et al.* [120] observed that soil carbon stabilization was related more to the sesquioxides content than to the clay types or their relative specific surface areas. In a study on the relationship between different soil minerals (Illite, Smectite, Chlorite and Kaoli-

nite) with SOC, Zeraatpische and Khormali [117] observed that illite and chlorite contents were significantly correlated with SOC, while smectite and kaolinite were not. This observation is explained by the fact that illite and chlorite develop high amphoteric properties in their ruptured edges, which absorb the OC [115]. Zeraatpische and Khormali [117] suggested that kaolinite showed the least correlation with SOC due to its small specific surface area. Contrary to the results of Zeraatpische and Khormali [116], Jindaluang *et al.* [112] analysed several mineralogically contrasting soils and observed that smectitic soils tend to have more OM content than kaolinitic ones. Schulten and Leinweber [122] have summarized a quantitative relationship between clay mineralogy and OC which can be used to deduce possible effects of clay mineralogy on the OC contents of organic-mineral clay fractions (Table 1).

Table 1. Clay contents, predominant clay minerals and OC contents of organic-mineral clay fractions.

Clay content (%)	Predominant clay minerals	OC content	Soil type
60	Smectite	2	Calcareous Grumusol (Calcic Vertisol)
39	Kaolinite and smectite	1 - 2	Alluvial soil (Fluvents)
32	Allophane	13 - 14	Humic Allophane soil (Typic Dystrandept)
6	Smectite, less vermiculit	e 6	Orthic Ferro-Humic Podzol (Orthic Spodosol)
17	Chlorite (vermiculite, illite)	11	Humic Eluviated Gleysol (Humaquepts)
3 - 15	Illite (vermiculite)	4 - 16	Typic Ustochrept, Udic Haplustalf, Dystric Cryochrept, Typic Cryorthod, Typic Dystrochrept, Haplic Cryohumod
8	Smectite	15	Xeralfic Haplargid
17 - 18	Kaolinite	2 - 3	Merredin Sandy Loam (Ustalfs)
8 - 45	Chlorite-mixed layers	1 - 20	Haplohumult, Argixeroll, Durargid, Andep
45	Smectite	2	Pelloxerert
17	Kaolinite and illite	2 - 6	Rhodoxeralf
45	Smectite and illite	7 - 9	Haploboroll
46	Palygorskite	3 - 7	Calciaquoll
69	Smectite	1 - 2	Dystric Gleysol (Tropaquepts)
8	Illite, less smectite	4 - 6	Orthic Greyzem (Orthic Mollisol)
9	Chlorite-mixed layers	8 - 11	Dystric Cambisol (Dystropepts)
9	Illite (quartz, feldspars, smectite)	8 - 9	Typical Hapludalf
2	Smectite	6 - 17	Haplic Albeluvisol (Typic Haplocryalfs)
28	Smectite/vermiculite	2 - 5	Typic Paludalf, Typic Hapludalf

Source: Adapted from [122]. For consistency of classification, soils classified in other systems other than the U.S. Soil Taxonomy have been classified according to the U.S. Soil Taxonomy (2003) based on their approximate correlations, as established by [119].

Table 1 shows that soil fractions rich in kaolinite contain small amounts of OC whereas chlorite-rich clay fractions contain large amounts of OC. This difference in SOC content is explained by the low pH in the chlorite-rich clay fractions which favours the formation of secondary chlorites and inhibits the decomposition of OM [122]. Additionally, it is observed that smectite-rich fractions contain OC contents within a wide range, with the largest values in soils poor in clay contents. According to Schulten and Leinweber [122], the adsorption capacity of different clay minerals for OM may vary, depending on factors such as clay content and mineralogy, chemical and biological soil properties, vegetation type (as major driver of carbon inputs to soil), and soil management (in terms of manuring or organic residue removal) among other factors. The different soil types in the table above account for the variations observed in clay content, organic carbon and type/quantity of clay minerals. Additionally, it has been shown that environmental factors such as temperature and moisture could affect the carbon protection capacity of various clay types in soil [120]. Recently, it has been shown that mechanisms favouring mineral availability in soil, and hence the formation of the so-called short-range-ordered phases, are the key regulators of soil C storage [123] [124].

4. Influence of Clay Minerals on Soil Physical Properties

Soil physical properties such as texture, structure, moisture content, pore size distribution, plasticity, shrink-swell potential, soil strength and erodibilty affect every aspect of soil fertility and productivity. Soil physical properties determine the ease of root penetration, water availability and the ease of water absorption by plants, the amount of oxygen and other gases in the soil, lateral and vertical movement of water through the soil, and nutrient cycling [125]. Most of these properties are influenced to a large extent by the mineralogical composition of the soil. Particle size distribution results from the physical degradation of soil minerals due to imperfect lattice energy distributions in the silicate layers causing strains in the mineral structure [24]. Soil strength, aggregation and plasticity are affected by the various attractive and repulsive forces exerted by the various minerals. The overall structure of the soil is the product of the arrangement and bonding of individual soil particles into aggregates caused by ionic, organic, water and clay mineral surface interactions [126]. According to Schulten and Leinweber [122], clay mineralogical properties that influence aggregation are surface area, CEC, charge density, dispersivity and expandability. Non-crystalline clay minerals, such as allophane and imogolite, have high surface areas, and highly variable and pH-dependant charge properties that generally increase aggregation [127]. Non-expanding variable-charge crystalline clays, such as kaolinite (1:1), have low CEC and low surface area, which tend to decrease aggregate stability, while high activity clays such as smectites (Ca-smectites) and other 2:1 clays, which are associated with high CEC and large surface area, tend to increase aggregation [122]. It has been reported that the functional role of clay minerals in

soil is the formation of microaggregates [110] [124] [128] [129] [130] [131] and these microaggregates greatly influence phosphorus adsorption and availability in soil [132] [133].

According to Nelson et al. [134], the interaction of clay mineralogical properties such as CEC and surface area with soil organic carbon influences soil dispersivity wherein less reactive clays, like kaolinite, are less dispersive, while high activity clays like smectites (Na-smectites) are highly dispersive. Soil water retention characteristics are also influenced by the clay mineralogical make-up of the soils [135], due to variations in specific surface area and solute-water-solid interactions of specific clay minerals. Soil erodibility is also affected by mineralogical composition because the mineralogy of the soil influences such properties as aggregate stability, permeability and soil shear strength [136] [137]. Ramezanpour et al. [62] observed that landscapes dominated by smectite group and double layer clay minerals that are dispersive (2:1 clays), such as Na-smectites, are more susceptible to soil loss by erosion, leading to the formation of gullies and badlands. Heshmati et al. [138] carried out a comparative study to evaluate the effects of soil and rock mineralogy on soil erosion and fertility status in Iran and observed that soils rich in calcite, dolomite, quartz and kaolinite were moderately resistant to erosion with the formation of inter-rill, rill and snow erosion, producing a moderate soil erosion intensity (5 - 10 t·ha⁻¹·yr⁻¹ of soil loss) whereas mica/smectite clay minerals produced gully erosion and considerable soil loss (>12.0 t·ha⁻¹·yr⁻¹ of soil). Equally, soils rich in smectite were found to promote landslide occurrences and severe annual soil loss (>16 t·ha⁻¹·yr⁻¹) [138].

Surface soil loss by erosion has been a major constraint to soil productivity in sub Saharan African countries. The direct effects of soil erosion on soil fertility status are reduction in topsoil thickness, alteration in soil properties, sedimentation and inundation of lowlands, and depletion of soil organic matter and nutrients. Additionally, eroded soils, with exposed sub-soil horizons, are prone to compaction because of high clay or gravel contents, and low organic matter contents. Hence, the exposed subsoil generally has higher bulk density and cone index, lower water infiltration rates, and higher runoff losses than uneroded soils. The resulting compacted soil alters soil tilth, limits root respiration and growth, and thus reduces crop production [32].

5. Influence of Clay Minerals on Soil Acidification

Soil acidity is one of the most important indices of soil health and almost all soil biochemical reactions are influenced by soil pH [139] [140] [141]. Soil acidity also conditions the activity, survival and growth of soil microorganisms [142]. With respect to soil fertility and crop production, clay minerals play an important role as they release various acidic species in the soil solution, which may significantly affect agricultural production [140] [141] [143] [144]. Acidic soils such as those of humid tropical environments generally have high concentrations of Al³⁺ and H⁺ originating from either acidic soil minerals [145] [146] or

acidic SOM [147] [148].

The natural acidification processes of these soils according to McBride [77] include: 1) removal of cations (Ca²⁺, NH₄⁺, Mg²⁺, K⁺ etc.) and anions (PO₄³⁻, NO₃⁻, SO₄²⁻ etc.) from soil by plant roots; 2) metabolic activity of roots, microorganisms, and other living organisms in the soil—these metabolic processes generate CO₂, soluble organic acids, and acidic organic residues, all of which behave as weak acids in the soil, displacing basic cations from exchange sites; 3) oxidation of reduced forms of S and N, 4) biological nitrification, and 5) dissolution of acidic gases from the atmosphere. Regarding the role of soil minerals on soil acidity, there exists a strong correlation between soil pH and Al³⁺ concentration.

Decreasing soil pH increases the instability of soil Al-minerals and thereby increases the concentration of total Al in solution [149]. These minerals are primarily Al oxides, gibbsite, feldspars, Al-rich allophanes, etc. When the pH is low (<5.5) the concentration of Al^{3+} in soil solution can be influenced by several processes such as; 1) a decreasing amount of variable charge on exchange sites, 2) exchange of Al^{3+} with H^+ , 3) hydrolysis of Al with resulting increase in the concentration of Al^{3+} , 4) dissolution of gibbsite and release of Al^{3+} [150]. Under advanced weathering conditions as is the case in most humid tropical soils, it is generally assumed that the activity of Al^{3+} is regulated by equilibrium with a gibbsite-like ($Al(OH)_3$) phase [150]. This solubility of Al depends on the solubility product (K_{sp}). Considering the case of gibbsite, the solubility product can be expressed as follows [150]:

$$Al[OH]_{3(s)} \leftrightarrow Al^{3+} + 3OH^{-}, K_{gibbsite} = [Al^{3+}][OH^{-}]^{3} = 10^{-32.64}$$
 (1a)

$$Al(OH)_{3(s)} + H^+ \leftrightarrow Al^{3+} + 3OH^-, K_{sp} = 8.5$$
 (1b)

Equation (1a) indicates that the activity of Al³⁺ in water depends on pH of the soil solution while Equation (1b) shows the dissolution of gibbsite in the presence of an acid or in acidic milieu. At pH values below 5.5, the concentration of Al³⁺ increases due to the increasing solubility of gibbsite [27]. Aluminium has a tendency to form hydroxy complexes, which can increase the solubility of gibbsite significantly. The total amount of dissolved Al in soil solution consists of both Al³⁺ ions and hydroxy complexes and can be described as a mass balance equation [77]:

$$Al_{dissolved} = Al^{3+} + Al(OH)^{2+} + Al(OH)^{+}_{2} + Al(OH)^{-}_{4} + Al_{complexes}$$
 (2)

At pH values below 5.5, aluminosilicate clays and Al hydroxide minerals begin to dissolve, releasing Al-hydroxy cations and Al³⁺ that then exchange other cations from soil colloids [77], especially the basic cations which are essential for plant nutrition such as Ca²⁺, Mg²⁺ and K⁺. The result is that the fraction of exchange sites occupied by Al³⁺ and its hydrolysis products can become large once the soil pH falls below 5.0, and the direct consequence of this high Al concentration in the soil solution is Al toxicity, which causes restricted growth of roots

and stems, leading to increased susceptibility to drought and decreased use of subsoil nutrients [151] [152] [153]. Toxicity of Al becomes very pronounced at very low pH when it is present in the mononuclear A1³⁺ species which exists as an octahedral hexahydrate [154] [155]. According to Sanchez and Logan [156], about one third of tropical soils (an equivalence of 1.7 billion hectares) are acidic enough for soluble aluminium to be toxic for most plants. Apart from toxicity, high Al concentrations also render phosphorous unavailable for plant uptake [157] [158]. This is because similar to Fe, Al becomes more accessible on cation exchange sites, in solution, or simply on exposed surfaces. Both ions react readily with phosphate, forming relatively insoluble compounds through the process of phosphate fixation [50] [158] [159].

$$AI^{3+} + 3H_2PO_4^- \leftrightarrow Al(H_2PO_4)_2, pH < 5.5$$
 (3)

The product formed in Equation (3) is insoluble in water and precipitates from solution. With time, the Al-phosphate complex becomes less soluble and less available to plants. In the case where Al originates from a mineral such as Kaolinite, exposed Al-OH groups (or the octahedral Al) react very fast with phosphates as follows [160]:

$$Al_2Si_2O_5(OH)_4 + 2H_2PO_4^- \leftrightarrow 2Al(OH)_2H_2PO_4 + Si_2O_5^{2-}$$
 (4)

Fixation of Al on cation exchange sites of soil colloids also means a reduction in cation exchange capacity. With respect to availability of soil nutrients, soil pH has great influence on plant nutrient availability, depending on the nature and behaviour of the nutrient element in different acidic media [161] [162]. Soil pH also affects biological activities of beneficial microorganisms such as bacteria, fungi and other soil microfauna [161]. Details of Al chemistry have been reviewed, where soil Al is reported to occur in many different forms as a function of soil pH [25] [27].

6. Influence of Clay Minerals on the Activity and Population of Soil Microorganisms

The activities of microorganisms in soil help to improve on its quality and fertility status [163] [164] [165] [166] [167], and hence the promotion of plant growth [168] [169] [170]. These organisms are imperative for maintaining the stability and productivity of agro-ecosystems [171]. In agricultural soils, these organisms play a role in the breakdown and mineralization of SOM, formation of humus, nutrient and elemental cycling, formation of soil aggregates, improvement of soil structure and water-holding capacity, biological nitrogen fixation, control of pests and diseases, climate regulation, promotion of plant growth and degradation of pollutants such as pesticides and hydrocarbons [172] [173] [174].

Soil microbial communities are greatly influenced and regulated by the environmental properties of their habitats. Soil pH, moisture, and temperature have been reported as the primary factors affecting soil biotic activities, wherein spe-

cific microorganisms have particular pH, moisture and temperature optima that influence their activities [175]-[180]. Other factors affecting biological activity in natural soils include nature of substrates (energy rich or poor substrates), anthropogenic activities (tillage type), soil aeration, light availability, microbial associations, quantity and quality of SOM, microclimate conditions and soil physicochemical properties [181]. Additionally, the type of nutrient management (chemical fertilizers and organic amendments) in agricultural soils can either improve or degrade soil microbial communities [182] [183] [184] [185].

The correlation between particle size fractions and microbial populations in soil has been reported [186], but the role of clay minerals on soil biological activity has obtained little interest in soil fertility studies. Within the soil system, microorganisms can readily influence the properties of clay minerals and can also act as a living catalyst in the geochemical cycles of clay minerals [169] [187]. Regarding nutrient uptake by plants, microorganisms have different strategies to improve Fe uptake of plants, notably through the release of organic molecules and metabolites (e.g. phytosiderophores, organic acids and flavonoids which form complexes with Fe (III) thereby solubilizing the Fe found in soil minerals) [188]. Other important macronutrients in soil such as K can be made available to plants through the dissolution of silicate minerals by microorganisms such as Acidothiobacillus ferrooxidans, Paenibacillus spp, Bacillus mucilaginosus, B. edaphicus, and B. circulans through mechanisms such as acidolysis, complexolysis, chelation and exchange reactions [170]. As concerns K nutrition, much work has recently been conducted to reveal the role of microorganisms on K solubilization and availability for plant growth within the soil system [31] [189] [190]. With respect to N, P, K and micronutrients dissolution, availability and uptake by plants, Burghelea et al. [174] and Terrazas et al. [191] have reviewed the various mechanisms involved in soil-plant-microbiota interactions.

Through a variety of mechanisms such as reduction and oxidation of structural iron, mineral dissolution and precipitation, particular minerals with specific chemical compositions and properties may in turn influence microbial communities in soil [192] [193] [194] [195]. Ransom et al. [196] observed that the most common mineral-biological interaction in soil was the close association (surrounding) of isolated heterotrophic bacterial cells by clay minerals and that the external surfaces of the bacteria were covered with secreted exocellular slimes composed of cross-linked polysaccharide fibrils which act to bind mineral particles into relatively robust microaggregates (roughly <25 µm in diameter). In earlier studies, Filip (1973) reported the beneficial effects of bentonite on the growth of some soil microflora. Kostka et al. [197] demonstrated that pure cultures of Shewanella oneidensis strain MR-1 as well as enrichment cultures of Fe (III)-reducing bacteria from rice paddy soil and subsurface sediments are capable of conserving energy for growth with the structural Fe (III) bound in smectite clay as the sole electron acceptor. Their results showed that growth with smectitic Fe (III) is similar in magnitude to that with Fe (III) oxide minerals and

is dependent upon the mineral surface area available, and thus concluded that Iron (III) bound in clay minerals acts as an important electron acceptor supporting the growth of bacteria in soils or sedimentary environments. Loveley and Phillips [198] also showed that microorganisms can completely oxidize organic compounds with Fe (III) or Mn (IV) as the sole electron acceptor and that oxidation of organic matter coupled with dissimilatory Fe (III) or Mn (IV) reduction can yield energy for microbial growth. Thus, the presence of Fe and Mn bearing minerals in soil serve as energy substrates for growth of some microorganisms. Stotzky and Rem [199] reported that the respiration of 27 fungal species was generally not affected by pH whereas the increase in concentration of montmorillonite (>4%) significantly inhibited microbial respiration and promoted the growth of Bacillus subtilis, Bacillus megaterium, Proteus vulgaris and Pseudomonas sriata as a result of the buffering ability of this clay mineral to maintain the pH at levels adequate for sustained microbial growth. On the other hand, kaolinite played a similar role to montmorrilonite only at concentrations above 40%, owing to the smaller specific surface and lower viscosity of koalinite compared to that of montmorillonite. It has also been observed that kaolinite and montmorillonite stimulate the exponential growth of Bacillus thuringiensis in a nutrient-rich medium due to the accumulation of nutrients on the surface of the clay particles through mechanisms of cation exchange and ligand bond processes [200]. Courvoisier and Dukan [201] investigated the effect of kaolinite on various growth parameters of Escherichia coli and observed that kaolinite significantly affected maximal growth rate and yield of the E. coli strain—(MG 1655) in minimum growth medium with 0.2% glucose, at an optimal concentration of 0.2 to 0.5 g/l. Carson et al. [202] also observed that the addition of minerals (such as mica) and rocks (such as basalt and rock phosphate) caused significant changes in the bacterial community structure, due to the creation of nutrient-rich hotspots in soils, which increased the relative abundance of the microorganisms.

Under artificial soil conditions, Ding *et al.* [181] investigated the influence of clay minerals (montmorillonite and illite), metal oxides (ferrihydrite and gibbsite) and charcoal on soil bacterial communities and observed that montmorillonite and illite significantly influenced *Bacteria* and *Beta proteobacteria*, while a weak influence of metal oxides on *Beta proteobacteria* was obtained. Contrary to enhancing microbial communities and activity, clay minerals have also been reported to inhibit the growth and activity (respiration) of soil microorganisms [195] [200] [203] [204] [205]. For example, Wong *et al.* [204] observed that clay minerals (notably bentonite and kaolinite) have the potentials to inhibit the sulphate-reducing ability of *Desulfovibrio vulgaris* in sediments, and proposed that such inhibition might be due to the direct effect of Al³⁺ on the bacteria. Also, Rong *et al.* [200] observed that kaolinite and montmorillonite inhibited sporulation of *Bacillus thuringiensis*, while goethite hindered sporulation and significantly depressed the total metabolic activity of the bacterium. Lavie and Stotzky

[203] reported that kaolinite, montmorillonite and polygorskite reduced the rate of respiration of *Histoplasma capsulatum*, through mechanisms of adhesion with mycelial surface which interfere with the movement of nutrients, metabolites, and gases across the mycelia wall. Details of the different mechanisms of bacterial adhesion by clay minerals have been reported in other studies [206] [207] [208] [209] Savage. Most recently, it has been demonstrated that structural Fe (II) from the reduction of Fe (III) in clay minerals (such as nontronite) appears to be the primary source of ·OH radical, which causes the death of some microorganisms.

7. Conclusions and Future Challenges

This study sought to demonstrate how clay minerals influence soil fertility and plant growth through its direct impacts on soil physical, chemical and biological properties. The relevant literature that has been selected and discussed in this work indicates that studies on the physical and chemical properties of clay minerals are not only of academic or theoretical interest, but have immense practical applications in soil fertility management and crop production. Based on the literature review presented in this work, state-of-the-art information concerning the subject matter is hereby succinctly presented. First of all, mechanisms of nutrient retention, release and availability have been well documented in the literature, yet are not completely understood. Most of these mechanisms involve adsorption-desorption and dissolution-precipitation processes. Secondly, mechanisms of SOM retention and stabilization by clay minerals have also been well documented but are not definite. Notwithstanding, it is probable that mechanisms leading to the formation of short-range-ordered phases [123], which act as regulators of soil C storage, form the basis for understanding SOM retention by clay minerals. Besides this mechanism another commonly acceptable means of SOM stabilization involves organo-Fe complex formation or tertiary associations among iron oxides, OM and other soil minerals, which overrules sorption mechanisms that were generally accepted in earlier studies. As concerns the influence of clay minerals on N, P and K retention and availability in soil, a vast majority of studies have been directed towards K nutrition, followed by P and lastly N. Furthermore, clay minerals affect soil physical properties primarily through the formation of microaggregates, which in turn influence nutrient availability and plant growth. In fact, it has been established that the most important role of clay minerals vis-à-vis soil fertility, is the formation of microaggregates. With regards to soil acidification, a soil's pH as influenced by clay minerals is a rather straight forward concept, this as a result of the nature of different clay minerals (i.e. either basic or acidic) within particular environments. Based on knowledge about nutrient sequestration by clay minerals, recent advances have been made in promoting nutrient availability and uptake through the use of nutrient-solubilizing microorganisms, especially K and P.

For future research, it will be imperative that clay mineralogy and soil biology

be given equal weight when conducting soil fertility studies. This automatically requires the need for developing expertise in the both disciplines. Given that mineralogical analyses are indispensable in soil fertility investigations and for developing effective fertilizer recommendation systems, the major challenge for scientists is the development of rapid, low-cost, reliable and efficient techniques of soil mineralogical analysis directly applicable to soil fertility investigations and management. Future research should also investigate mineralogical factors that will favour the sequestration and quantification of soil N across different climatic gradients and ecosystems, in a similar way to the great interest that had been directed towards carbon. This could be very helpful not only in sustaining soil health and crop production, but also contribute in mitigating climate change. Additionally, there is need to understand how changes in mineralogy will affect nutrient budgets and how these changes can influence soil testing methods and their interpretations. Also, it is our desire that this overview stimulates expert research that can develop quantitative correlations among clay minerals, soil fertility attributes and plant growth such that a more simplified and clearer image is discerned.

Lastly, clay minerals should find a place within the concept of soil quality. Soil quality is a very important concept in soil science and was established in an attempt to balance multiple soil uses with goals for environmental quality [210]. Unfortunately, the concept has been a source of division among soil scientists due to its many weaknesses and contradictions [211], especially when it comes to the choice of soil quality indicators and methodologies used for establishing soil quality indices. In most studies that have attempted to define soil quality and establish soil quality indices [212] [213] [214] [215], it is unfortunate that clay minerals have been overlooked. This is probably because most desirable soil quality indicators are those attributes that are most sensitive to management [216]. Given that clay minerals have a great role to play in different soil ecological functions, they need to be considered and incorporated within soil quality indicators. As already observed in soil science, this task must incorporate the joint efforts of different research fields such as interfacial and colloid chemistry, clay mineralogy, soil science, plant physiology and soil ecology.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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