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Original Research

Evaluation of the Continuous Application of Different Organic Materials on Soil Surface Charge and Chemical Properties Along the Soil Profile of a Typical Mollisol

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Abstract

Innovative agricultural technologies such as organic fertilization have provided long and short-term benefits as far as sustainable soil management is concerned. In this study, five treatments were applied: cow manure (CM), chicken manure (JM), poplar tree leaves (TL), maize straw (MZ), and control (CK). The aim was to evaluate the long-term effects of applying organic materials on soil chemical and electrochemical properties. The highest pH and EC were recorded in JM and CM respectively. The highest cation exchange capacity (CEC) and specific surface area (SSA), were recorded in treatment TL while the application of organic materials increased the CEC and SSA by 24.9-85.5% and 6.9-52.4% respectively. The surface charge characteristics were significantly improved by the organic treatments compared with CK ($P<0.05$). The application of organic materials increased the surface charge potential ($\varphi 0$) by 28-35.9% and the surface charge density ($\sigma 0$) by 21.42-35.71%. Moreover, the electric field strength (E0) and surface charge number (SCN) were increased by 16.6-27.8% and 21.7-94.9% respectively. The soil chemical and electrochemical properties decreased along the soil profile with the exception of pH and EC, which increased with depth. The granulometric properties of organic matter and other physical attributes affected the chemical and electrochemical properties of the soil. The surface charge characteristics were significantly positively correlated with each other and the soil chemical properties as shown by the correlation analysis. The application of organic materials especially treatment TL is recommended as it had a more advantageous effect on enhancing the surface charge characteristics and could improve the quality of agricultural soils.

Keywords: organic materials, chemical properties, surface charge properties, organic matter, soil profile

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Introduction

In considering the major resources that support plant growth and development, soil is an important factor that cannot be neglected [1]. However, the intrinsic characteristics of the soil including the biological, chemical, and, physical features greatly affect the ability of the soil to perform its functions in supporting the development and growth of crops [2]. The chemical and electrochemical properties influence the processes that occur on the surface of soil particles [3, 4]. Specific surface area, electric field strength, charge density, and quantity of charges are important attributes that affect the surface charge properties (electrochemical properties) of soil [5]. They serve as indicators for evaluating the fertility and quality of agricultural soils [6]. The surface charge properties are strongly correlated with other soil processes such as the formation of soil structure and other organomineral complexes, movement of ions and water in the soil, plant nutrition, and the swelling, flocculation, dispersion, and shrinkage of the soil fractions [7] whiles soil chemical attributes such as EC, pH, etc. also affect the functions, productivity, and fertility of the soil [8-10]. Previous studies [11, 12] reported that organic matter contents, clay mineralogy, particle size distribution, pH, and land-use activities are important intrinsic and extrinsic features that greatly affect surface charge properties.

Several studies have detailed the beneficial results of applying organic materials on soil humic fractions and structural characteristics, physicochemical properties, microbial biomass, abundance, and diversity [13-17]. However few of these studies have specifically analyzed the beneficial effects of different organic materials applications on soil surface charge properties as far as the electrochemical properties of soil are concerned. Moreover, few of these studies have analyzed the effects of the surface application of the organic materials on the subsurface soil properties. Other studies that tried to analyze the effects of organic amendments on the electrochemical properties of the soil were based on short-term studies that created inconsistencies in results. Knowing how the chemical and electrochemical properties directly influence other functions of the soil, and how the and surface charge characteristics provide insights into the biochemical, chemical, and physical functions and processes in the soil [18-21], it is, therefore, imperative to study to understand how applications of organic materials improve or affect the chemical and electrochemical properties of soil for agricultural development.

This study explored how the chemical and electrochemical properties of soil vary and their relationships under different organic material treatments along the soil profile after long-term applications. The hypothesis was that the chemical and electrochemical properties and their relationships with depth will vary with the application of different organic materials. To test the hypotheses, the soil chemical and electrochemical properties under the different organic material treatments in Northeastern China were investigated. Consequently, the main objectives of this study were to: (1) investigate how soil chemical and electrochemical properties vary under the different organic material treatments; (2) explore the effect of the different organic material treatments on soil chemical and electrochemical properties along the soil profile; and (3) analyze the relationship between the chemical and electrochemical properties observed in this study. The results of this study are expected to provide key information about how the chemical and electrochemical properties of this soil are affected under long-term organic fertilization. This information would help to support the reasonable management and utilization of soil resources and also help to facilitate and reconstruct strategies for improving soil properties for sustainable agricultural development.

Materials and Methods

Site Study

The study was conducted at the Jilin Agricultural University Research Farm in Northeast China (43°48′N, 125°23′E; km). The climate of the area is a typical continental temperate monsoon. The effective accumulated temperature and the average precipitation are about 2950-3500ºC and 500-600 mm/year respectively. The soil in the area was classified as Udic Mollisol (according to the soil taxonomy of the USA) [15].

Experimental Design

The experiment was performed in 2010-2020 and it included a randomized block design consisting of 15 plots, 25 m^2 (5 m × 5 m) with five treatments in three replicates. The treatments for the study included an annual application of chemical fertilizer and organic amendments at the surface layer of the soil (0-20 cm). The treatments were: control (CK), chicken manure (JM), and cow manure (CM), maize straw (MZ), and poplar tree leaves (TL). The chemical fertilizers were applied at a rate of 165 kg of N, 82.5 kg of P, and 82.5 kg of K ha^{-1} per year. Application rates of organic materials were adjusted to similar amounts of organic matter (2000 $kgha^{-1}$). As such, the application rates of organic materials were 5036 kg/hm^2 chicken manure, 3892 kg/hm^2 cow manure, 2400 kg/hm^2 maize straws, and 3212 kg/hm^2 poplar tree leaves. The organic materials were repeatedly applied every year, usually in April-May, followed by the planting of soybeans. Table 1 shows the basic chemical properties of the different organic materials used in this experiment.

Table 1. Chemical properties of the organic materials used in this experiment.

Organic material	pH	Organic matter $/(g\ kg^{-1})$	Lignin/N	Total N $/(g\ kg^{-1})$	Total P $/(g\ kg^{-1})$	Total K $/(g\ kg^{-1})$	C/N ratio
Maize straw (MZ)	6.42±0.2	493±0.6	8.65±0.43	8.33±0.1	1.12±0.1	12.34±0.1	56.31±0.3
Cow manure (CM)	7.27±0.1	302±0.4	2.65±0.19	13.9±0.1	3.60±0.1	8.32±0.1	12.63±0.2
Chicken manure (JM)	8.03±0.3	240.11±0.5	1.51±0.32	17.07±0.2	8.79±0.2	14.09±0.2	14.21±0.1
Tree leaf (TL)	6.14±0.2	371±0.1	13.19±0.92	9.91±0.2	1.02±0.1	4.05±0.1	39.51±0.1

Note: values presented are means and ±standard error. Mean values in the same row followed by the same superscript for the different treatments are not significantly different at P<0.05.

Soil Sampling

In June 2020 (after 10 years of organic fertilization), soil samples were taken from each of the treatment plots. In each plot, three sampling points were randomly selected. Soil samples were collected from three different depths of the soil (0-20 cm, 20-40 cm, and 40-60 cm depths), using a core sampler then taken to the laboratory for soil physicochemical properties analysis.

Soil Laboratory Analysis

The bulk density of the soil samples was analyzed on undisturbed samples which were collected using the core sampling method as described by [22]. Using this method, soils were sampled or collected by drilling the core sampler into the soil. The core samples collected were oven-dried and the bulk densities were calculated by dividing the masses of the oven-dry soils by their respective volumes. The volumes will be determined by the volume of the core sampler used for the sampling.

Bulk density (BD) of the soil was calculated as;

$$\frac{mass\ of\ oven\ dry\ soil(g)}{volume(cm^3)}$$

Soil porosity was determined from soil particle density and bulk density using the equation shown below [23];

$$\text{porosity (pt)} = 1 - \frac{bulk\ density\ (pb)}{particle\ density(pd)} * 100\%$$

...where particle density was estimated to be 2.65 g/cm^3.

The hydrometer method was used to determine soil particle size distribution [24] while the organic matter (SOM) was determined using the $K_2Cr_2O_7$ external heating method [25]. Soil pH was determined using a glass electrode pH meter at a soil to water ratio of 1:2.5 [26]. Electrical conductivity (EC) was determined using a conductivity meter in a soil-water extract method [27]. Soil cation exchange capacity (CEC) was determined by the ammonium acetate method.

The soil surface charge properties and SSA were determined by following the methods described by Li et al. [21]. In this method, hydrogen saturated soil samples were used by firstly washing the soil samples (40 g for each treatment and the replicates) with 100 mL of 0.1 molL^{-1} HCl and the washing was repeated four times. Afterward, the samples were washed four times with the same volume of deionized water until the suspension was free of Cl$^-$ ions. The suspended (hydrogen saturated) soil was oven-dried at 60ºC. 5 g of the dried samples were weighed into a bottle followed by adding 55 ml of 0.01 molL^{-1} Ca(OH)2 and 0.01 molL^{-1} NaOH 1:1 mixed solution. The solution was shaken for 24 hours after which 1 molL-1 HCl was added in drops to adjust the pH to 7. The supernatant was collected followed by analyzing the concentration of Na$^+$ and Ca^{2+} with a flame photometer and an atomic absorption spectrometer respectively. The surface charge properties and SSA were measured using the equations proposed by Liu et al. [28] and Bao [29].

$$\varphi_0 = \frac{2RT}{(2\beta_{Ca} - \beta_{Na})F} \ln \frac{a^0_{Ca} N_{Na}}{a^0_{Na} N_{Ca}} \quad (1)$$

...where φ_0 (mv) is the surface potential, R and T(K) are the gas constant and absolute

Temperature (298), respectively; F (Cmol^{-1}) is the Faraday Constant; β_{Na} and β_{Ca} are the corresponding charge coefficients of Na$^+$ and Ca^{2+} respectively, and is calculated as β_{Na} = 0.0213 ln($I^{0.5}$) + 0.766, β_{Ca} = -0.0213 ln($I^{0.5}$) + 1.2331, where I is the ionic strength (molL^{-1}). a^0Na and a^0Ca (molL^{-1}) respectively represent the equilibrium activity of Na$^+$ and Ca^{2+} in bulk the solution; N_{Na}, and N_{Ca} (molL^{-1}) respectively represent the adsorbed quantities of Na$^+$ and Ca^{2+} at equilibrium.

The surface charge density σ_0 (Cm-^{2}) was calculated as follows:

$$\sigma_0 = \mathrm{sgn}(\varphi_0)\sqrt{\frac{\varepsilon RT}{2\Pi}\left(a^0_{Na} \exp(-\frac{\beta_{Na} F\varphi_0}{RT}) + a^0_{Ca} \exp(-\frac{2\beta_{Ca} F\varphi_0}{RT})\right)} \quad (2)$$

...where ε is the dielectric constant for water at room temperature.

$$E_0 = \frac{4\Pi}{\varepsilon}\sigma_0 \tag{3}$$

...where E_0 ($V\cdot dm^{-1}$) is the electrostatic field strength at the surface

$$SSA = \frac{N_{Na}k}{ma_{Na}^{0}}\exp\left(\frac{\beta_{Na}F\varphi_0}{2RT}\right) = \frac{N_{Ca}k}{ma_{Ca}^{0}}\exp\left(\frac{\beta_{Ca}F\varphi_0}{2RT}\right) \tag{4}$$

...where SSA ($dm^2\cdot g^{-1}$) is the specific surface area; κ (dm^{-1}) is the Debye parameter; $m = 0.5259 \ln(c^0_{Na}/c^0_{Ca}) + 1.992$, where c^0_{Na} and c^0_{Ca} respectively denote the concentration of Na^+ and Ca^{2+}

$$SCN = 10^5\frac{SSA\sigma_0}{F} \tag{5}$$

...where SCN ($cmol\cdot kg^{-1}$) denotes the surface charge number.

Statistical Analysis

Data on soil physicochemical properties under the different organic amendments were collected. The data were subjected to statistical analysis using ANOVA (Analysis of Variance). Duncan's new multiple range tests were used for multiple comparisons to compare treatment means to test their significance in variation. All data analysis was done using Microsoft Excel 13.0 and SPSS 23.0.

Results and Discussion

Basic Soil Physicochemical Properties under the Different Treatments along the Soil Profile

The basic soil physicochemical properties under the different treatments along the soil profile are shown in Table 2. After analyzing the effects of the different treatments and depth on the bulk density of the soil, the results showed that the different treatments, depth, and interaction (treatments * depth) had a significant effect on bulk density ($P<0.05$). Moreover, bulk density increased significantly with depth ($P<0.05$). In the 0-20cm depth, the results showed that the highest bulk density was recorded in CK (1.41 g/cm^3) and the lowest was recorded in MZ (1.27 g/cm^3) as some research works have proved that organic amendments increased soil physical fertility, mainly by improving aggregate stability and decreasing soil bulk density [30, 31]. The increase in organic matter content through the annual additions of fresh organic matter lowered the bulk density by creating more spaces for the flow of air and water as similarly reported by Oo et al. [32] and Wang et al. [33]. Similarly, due to the inversely proportional relationship between porosity and bulk density, the highest porosity was recorded in MZ (51.82 %) and the lowest in CK (46.53%). The application of the different organic materials to the surface of the soil reduced bulk density and increased the porosity by 0.24-9.9% and 0.27-11.36% respectively ($P<0.05$). This was due to the much lower intrinsic density of the maize straws and tree leaves hence soils receiving these organic amendments showed a decrease in dry bulk density and increased soil porosity [34]. Moreover, the effects of organic amendments on soil porosity may also occur indirectly through their influence on soil fauna (e.g., earthworms) whose feeding and burrowing activities modify porosity [35]. Udom et al. [36] and Luna et al. [37] reported similar findings.

The texture of soil is known to be a soil property that takes time to change amid soil management practices [23]. The different organic treatments affected soil particle size distribution where the highest clay and silt were recorded in the organic amended fields and the highest sand was recorded in CK which was significantly different from the other treatments ($P<0.05$). This could be due to the high organic matter content which causes clay and silt particles to bind to organic matter due to their mineralogy and surface charge properties [38, 39]. This improves the adsorption of organic compounds and molecules to the clay surfaces thereby making the clay particles more organophilic and hydrophobic and therefore not easily washed away from the soil surface [40, 41]. The high CEC of the organic matter found in the amendments could also be a reason for this observation [42]. The general distribution of soil particles for typical millisols is known to contain high silt and clay as reported by Ghiberto et al. [43] and Meimaroglou and Mouzakis [42]. As such the findings of this study did not differ much from that of a typical mollisol. Moreover, the results showed that depth had a significant effect on the distribution of soil particles however the interaction (treatment * depth) did not affect the distribution of sand and silt ($P>0.05$). Among the organic treatments, the highest clay percentage was recorded in MZ (38.26%) however it was not significantly different from CM and JM ($P<0.05$). Though in the 0-20cm layer, the highest percentage of silt was recorded in CM (32.57%), there was no significant difference between the percentage of silt among all the treatments. The percentage of clay and silt in the organic plots was 1.18-2.97% and 0.66-1.34% respectively higher than CK while the percentage of sand was 2.46-4.1% lower than CK.

After analyzing the effects of the different treatments and depth on SOM, the results showed that the different treatments, depth, and interaction (treatment * depth) had a significant effect on SOM ($P<0.05$). For the surface layer, the highest SOM values were recorded in the organic-amended plots which were all significantly higher than CK ($P<0.05$). However, among the organic treatments, there was no significant difference between the SOM values in treatments JM and CM ($P<0.05$). This observation was mainly attributed to the enhanced aggregates stability which improved the soil structure

Table 2. Soil physicochemical properties under different treatments along the soil profile.

Treatments	SOM (g/kg)	Bulk density (g/cm^3)	Porosity (%)	Clay (%)	Sand (%)	Silt (%)
0-20 cm						
CK	16.37^{d}±0.10	1.41^{a} ±0.00	46.53^{d}±0.33	35.29^{c}±0.16	33.47^{a}±0.22	31.23^{a}±0.08
TL	20.17^{a}±0.04	1.30^{bc}±0.01	50.68^{ab}±0.66	36.47^{b}±0.24	31.01^{b}±0.28	32.51^{a}±0.36
JM	17.70^{c}±0.11	1.35^{b}±0.02	48.79^{c}±0.76	38.07^{a}±0.09	29.58^{bc}±0.12	32.34^{a}±0.18
MZ	19.50^{b}±0.06	1.27^{d}±0.00	51.82^{a}±0.33	38.26^{a}±0.18	29.84^{bc}±0.78	31.89^{a}±0.90
CM	17.50^{c}±0.11	1.41^{a}±0.02	46.66^{d}±0.82	38.06^{a}±0.13	29.37^{d}±0.62	32.57^{a}±0.72
20-40 cm						
CK	14.5^{d}±0.10	1.47^{a}±0.01	44.49^{c}±0.41	36.61^{d}±0.19	32.57^{a}±0.12	16.37^{a}±0.10
TL	19.6^{a}±0.15	1.34^{c}±0.01	49.18^{a}±0.45	39.67^{c}±0.33	30.73^{b}±0.16	20.17^{a}±0.04
JM	16.33^{c}±0.17	1.40^{b}±0.02	47.16^{b}±0.78	41.17^{ab}±0.16	29.66^{bc}±0.47	17.70^{a}±0.11
MZ	18.60^{b}±0.11	1.33^{c}±0.00	49.68^{a}±0.33	40.63^{bc}±0.34	28.89^{cd}±0.82	19.50^{a}±0.06
CM	16.43^{c}±0.14	1.46^{a}±0.01	44.65^{c}±0.54	49.17^{a}±0.49	28.06^{d}±0.21	17.50^{a}±0.11
40-60 cm						
CK	12.8^{d}±0.23	1.51^{a}±0.01	42.88^{a}±0.54	40.30^{b}±0.18	23.73^{a}±1.3	35.95^{a}±1.46
TL	17.56^{a}±0.08	1.48^{a}±0.02	44.02^{a}±0.88	41.87^{a}±0.12	22.15^{a}±1.42	35.98^{a}±1.32
JM	15.33^{c}±0.08	1.49^{a}±0.01	43.51^{a}±0.66	42.69^{a}±0.17	22.0^{a}±1.83	35.11^{a}±1.87
MZ	16.9^{b}±0.17	1.45^{a}±0.01	45.15^{a}±0.45	42.15^{a}±0.75	21.76^{a}±1.27	36.08^{a}±0.85
CM	14.9^{c}±0.11	1.5^{a}±0.02	43.39^{a}±0.78	41.9^{a}±0.55	21.8^{a}±1.2	36.29^{a}±0.80

Note; values presented are means and ±standard error. Mean values in the same row followed by the same superscript for the different treatments are not significantly different at $P<0.05$.

and ability of soil to hold on to organic matter to reduce the further degradation of organic materials by soil microorganisms [44]. Among the treatments, the highest SOM was recorded in TL due to the higher polyphenols, lignin contents, and higher lignin/N ratios in TL which reduces the rates of decomposition thereby increasing the accumulation of SOM [14]. Several studies such as Hu et al., [14], Fan et al., [13], and Wu et al., [45] have reported similar results. In all, the SOM decreased with depth and the organic treatments increased the SOM content by 6.9-23.21%. The slight increase in SOC at the 20–40 cm layer in the amended plots may have been caused by the downward movement of the fine organic particles into the 20–40 cm. This movement is largely attributed to the soil faunal activities, water transport, and root-soil interaction [46]. SOM generally decreased with depth mainly because down the soil profile enzymatic activities reduce thereby reducing the production and conversion of SOM [47] as similarly reported by previous studies [48, 46].

Effect of Organic Materials on Soil pH

It is believed that the qualities of organic material can influence the pH of soil when applied as an amendment, such that if the amendment has a high pH, the pH of the soil will be affected in a likewise manner and vice versa [49]. After analyzing the effects of the different treatments and depth on the soil pH, the results showed that the different treatments, depth, and their interaction (treatment * depth) had a significant effect on soil pH ($P<0.05$) as shown in Fig. 1. The different organic materials had varying effects on soil pH however there was no significant difference between the pH of the organically amended plots ($P<0.05$). In the surface layer, the highest pH was recorded in treatment JM and the lowest was recorded in CK indicating that the different organic materials affected the pH of the soil. The overall pH changes in the 0-20 cm and 40-60 cm layer followed the order JM>CM>MZ>TL>CK while that of the 20-40 cm layer followed the order JM>MZ>CM>TL>CK. This is because cow manure, for instance, has a buffering and liming effect due to the presence of calcium carbonate in the amendment [50, 51]. Moreover, the high pH could be due to any of the following reasons; consumption of protons by functional groups associated with the organic materials during decomposition [52], the removal of carboxyl groups from the organic acids anions which also occur during consumption of protons [53], and the release of hydroxide ions from local anaerobic microsites during reduction reactions [54]. Similar results were reported

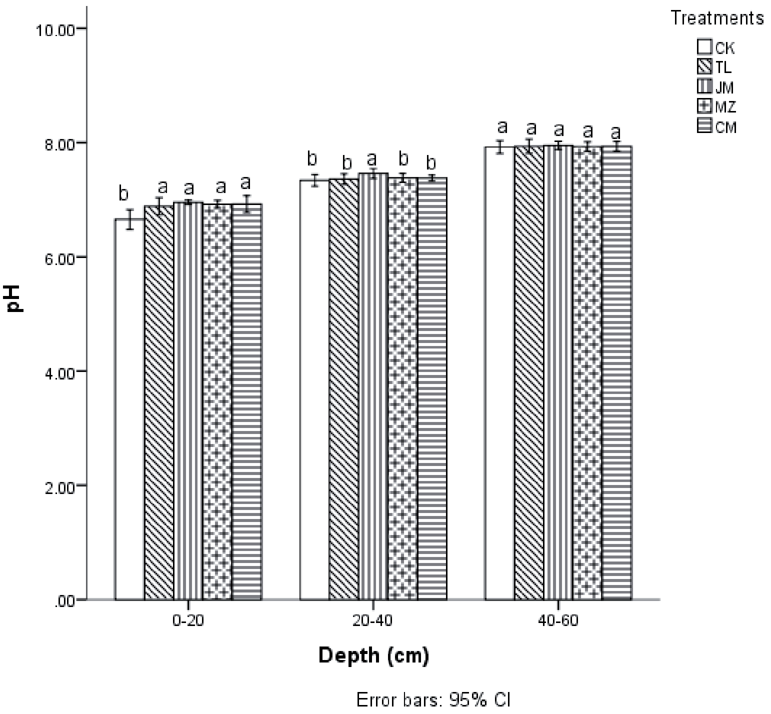

Fig. 1. Effect of organic materials on soil pH along the soil profile.

by [50, 33, 51]. In all compared with CK, the organic treatments increased the pH by 3.45-4.51% ($P<0.05$) while soil pH increased significantly with depth as shown in Fig. 1. This could be due to the reduced organic matter and accumulation of basic cations at deeper depths through the leaching from surface soil. Similarly, Fungo et al. [55] and Kumar et al. [56] reported high pH levels at the lower depth of soil under different land-use types.

Effect of Organic Materials on Soil EC

From the results, depth and the different treatments had a significant effect on soil EC ($P<0.05$) however their interaction (treatment * depth) did not affect the EC ($P>0.05$). From Fig. 2, EC increased with depth and also increased significantly under the different organic material treatments compared with CK which could be due to the high CEC, pH, and clay contents, which improves conductance through the release of soluble mineral nutrients that contain salt. This occurs through the process of solubilization and mineralization after the application of the organic amendments [57]. Similarly, Page-Dumroese et al. [58] reported that there was an increase in soil EC after the application of biosolids. The highest EC was recorded in treatment CM and the lowest was recorded in CK and the overall EC changes in the 0-20 cm, 20-40 cm, and 40-60 cm layer followed the order CM>MZ>JM>TL>CK, MZ>CM>JM>TL>CK, and MZ>JM>CM>TL>CK, respectively. Compared with CK, the organic treatments increased the EC in the surface layer by 18.18-36.26% ($P<0.05$). The increase in EC along the profile could be due to the increases in clay down the profile (Table 2) as fine-textured soil particles are known to have high EC [59, 60].

Effect of Organic Materials on Soil CEC

The results also showed that the different treatments, depth, and their interaction (treatment * depth) had a significant effect on soil CEC ($P<0.05$). The highest CEC values were recorded in the organically amended plots where TL had the highest followed by MZ however CEC decreased with depth. This may be a result of the many organic functional groups contained in organic materials and the dissociation of these acidic functional groups such as carboxylic and phenolic groups increased the soil negative charge and thus soil CEC [61]. The neutralization ability of the alkaline substances that were contained in the manure which led to a reduction in soil acidity and also increased the soil pH could also be a reason for this observation. The overall CEC changes in the 0-20 cm, 20-40 cm, and 40-60 cm layer followed the order TL>MZ>CM>JM>CK and the organic materials improved the CEC by 24.9-85.55% as shown in Fig 3. This is because although the same amount of carbon was applied however the high lignin in TL and MZ reduced their decomposability which improved the storage of organic carbon and organic matter thereby producing more variable charges and diverse cation substitution sites in the soil [6, 62]. In addition, the high silt and clay contents in the amended plots could also be a reason for the high SSA as Tang et al. [63] reported that smaller soil mineral particles usually contribute 76.1%

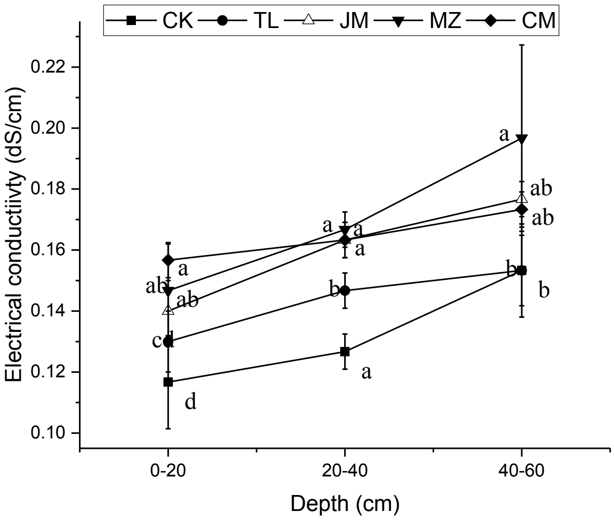

Fig. 2. Effect of organic materials on soil EC along the soil profile.

of the surface charges in soil. At increasing depths, the highest CEC was recorded in the organically amended plots because of the decomposition of the materials, which produces hydrogen ions and also increased the degree of organic matter oxidation. Similarly, Zhang et al. [64] reported that a decrease in pH resulted in a decrease in soil CEC. This helps to convert exchangeable base ions such as calcium, magnesium, sodium, etc. from soil colloids into soil solutions which can be leached out easily, and also cause an increase in CEC along the depths of the amended field [65, 66].

Effect of Organic Materials on Soil SSA

The specific surface area of soil (SSA) is considered an important attribute of the soil and it is highly related to the chemical and physical properties of soil especially the texture, hydraulic properties, and cation exchange with the soil matrix [67]. After analyzing the effects of the different treatments and depth on SSA, the results showed that the different treatments, depth, and their interaction (treatment * depth) had a significant effect on SSA ($P<0.05$). For the surface layer, the highest SSA values were recorded in the organic-amended plots which were all significantly higher than CK ($P<0.05$) which may be because the different organic matter released from the materials can change the surface properties of the soils by getting adsorbed to the soil surfaces [68]. This is done through the transformation process of the different materials which reacts differently to the soil surface thereby affecting the total area of the soil particle surfaces, improves the physical protection of organic carbon by soil particles (aggregates), and also enhances the hydraulic properties of the soil [69, 70]. Also, the higher clay and low sand contents coupling with the high organic matter (organic carbon) in the organic-amended plots could be a reason for the high SSA in the organic amended plots, as the sand particles are known to have high basic minerals but the clay particles tend to form colloidal-sized particles which have larger surface areas. Similarly, Tang et al. [63] reported that particles with diameters of less than 1 μm (usually clay particles) contribute 71.6% of the surface area of soil indicating that different soil particles have different mineralogical compositions which affect their surface characteristics. Sikora et al. [71] and Arthur et al. [72] also reported that the application of composts, biochar, and different manures increased the SSA of the soil. At the deepest depth, there was no significant difference between the SSA values in treatments TL and MZ ($P<0.05$). In all, SSA changes in the 0-20 cm, 20-40 cm, and 40-60 cm layer followed the order TL>MZ>CM>JM>CK. Moreover, SSA decreased with depth and

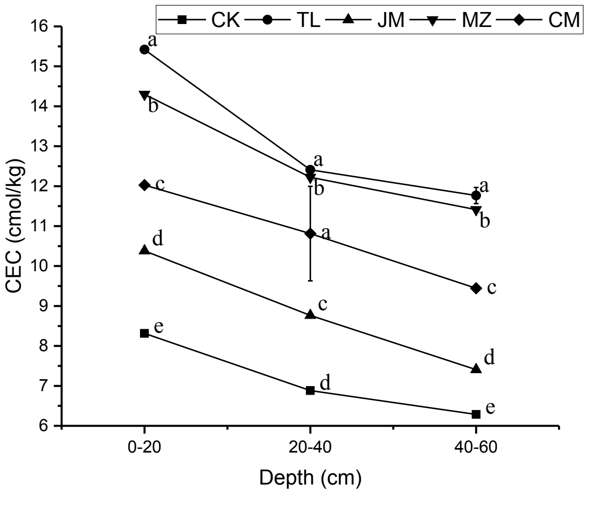

Fig. 3 Effect of organic materials on soil CEC along the soil profile.

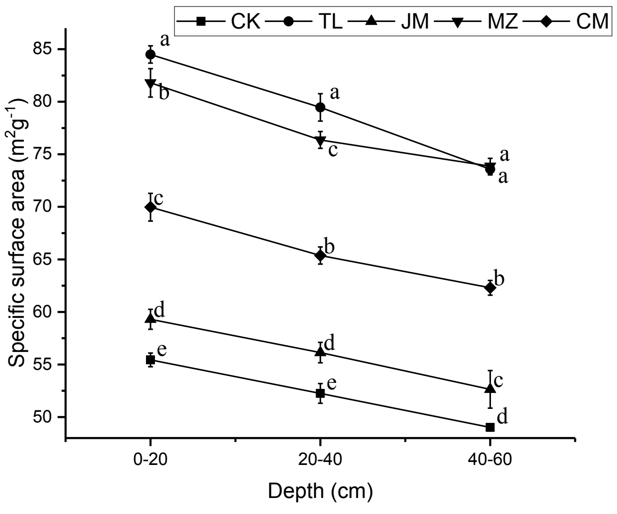

Fig. 4. Effect of organic materials on soil specific surface area along the soil profile.

the organic treatments increased the SSA content by 6.98-52.44% compared with CK (Fig. 4). This could mainly be due to the reduced organic matter along the profile as previous reports indicated that the removal of organic matter from the soil directly reduced the SSA of the soil due to a reduction in the content of soil organic colloids (which are known to have larger surface area than the inorganic minerals in the soil) [73, 74].

Effect of Organic Materials on Soil Surface Charge Characteristics

The soil surface charge characteristics varied significantly with the different treatments, depth, and their interaction (treatment * depth). The highest surface charge characteristics (surface potential, surface charge density, electric field strength, specific surface area, and surface charge number) were recorded in the organic-amended plots while the lowest was recorded in CK (Table 3). This was mainly attributed to the large production of organic colloids through the decomposition of the organic materials to produce organic matter. These colloids play a very important role in the soil by regulating the surface charge properties of the soil due to their high surface area. Most of the surface charge characteristics of soils are controlled by colloids. Studies such as Chen et al. [75] and Willgoose [76] have attributed the availability of soil colloids to soil organic matter contents on the surface of the soil. Moreover, at increasing depths, all the surface charge characteristics were reduced. For all the three different layers, the surface potential followed the order MZ >CM>TL>JM>CK whiles that of electric field strength followed the order TL>CM>MZ>JM>CK. The surface charge density and surface charge number all followed the same order of TL>MZ>CM>JM>CK. In all, the organic materials increased the surface potential, surface charge density, electric field strength, and surface charge number by 28.05-35.95%, 21.42-35.71%, 16.66-29.82%, and 21.76-94.94% respectively. Tang et al. [63] similarly indicated that colloidal-sized particles are essential factors that determine about 85% of soil surface properties. As such, the decrease in soil surface charge characteristics along the soil profile could be due to the reduced colloids and soil organic matter at different depths as similar findings were reported in previous studies [77, 78].

Correlation Analysis between Soil Properties

The correlation results showed that the soil chemical and electrochemical properties analyzed in this

Table 3. Soil surface charge characteristics at different depths under different treatments.

Treatments	φ_0 (mv)	σ_0 (Cm-^{2})	E_0 (Vm^{-1})	SCN (cmolkg^{-1})
0-20 cm				
CK	$-72.60^{d}\pm0.52$	$0.14^{d}\pm0.00$	$2.28^{d}\pm0.01$	$8.50^{e}\pm0.01$
TL	$-51.80^{c}\pm0.45$	$0.19^{a}\pm0.00$	$2.96^{a}\pm0.02$	$16.57^{a}\pm0.07$
JM	$-52.23^{c}\pm0.62$	$0.17^{c}\pm0.00$	$2.66^{c}\pm0.03$	$10.35^{d}\pm0.03$
MZ	$-46.50^{a}\pm0.94$	$0.18^{b}\pm0.00$	$2.80^{b}\pm0.01$	$15.15^{b}\pm0.08$
CM	$-48.66^{b}\pm0.53$	$0.18^{b}\pm0.00$	$2.83^{b}\pm0.03$	$12.88^{c}\pm0.02$
20-40 cm				
CK	$-78.60^{b}\pm0.40$	$0.12^{d}\pm0.00$	$1.97^{d}\pm0.02$	$6.83^{e}\pm0.03$
TL	$-54.36^{a}\pm0.31$	$0.18^{a}\pm0.00$	$2.83^{a}\pm0.03$	$14.65^{a}\pm0.03$
JM	$-54.90^{a}\pm0.73$	$0.16^{c}\pm0.00$	$2.50^{c}\pm0.03$	$9.25^{d}\pm0.05$
MZ	$-52.93^{a}\pm0.88$	$0.17^{b}\pm0.00$	$2.64^{b}\pm0.02$	$13.42^{b}\pm0.05$
CM	$-53.60^{a}\pm0.77$	$0.17^{b}\pm0.00$	$2.62^{b}\pm0.01$	$11.40^{c}\pm0.09$
40-60 cm				
CK	$-82.46^{d}\pm0.44$	$0.12^{d}\pm0.00$	$1.84^{d}\pm0.00$	$6.15^{e}\pm0.03$
TL	$-63.50^{c}\pm0.43$	$0.16^{a}\pm0.00$	$2.47^{a}\pm0.02$	$12.17^{a}\pm0.03$
JM	$-63.06^{c}\pm0.61$	$0.14^{c}\pm0.00$	$2.22^{c}\pm0.04$	$5.83^{d}\pm0.03$
MZ	$-59.36^{a}\pm0.31$	$0.15^{b}\pm0.00$	$2.35^{b}\pm0.03$	$11.40^{b}\pm0.02$
CM	$-60.90^{b}\pm0.51$	$0.15^{b}\pm0.00$	$2.33^{b}\pm0.02$	$9.58^{c}\pm0.08$

Note: values presented are means and ±standard error. Mean values in the same row followed by the same superscript for the different treatments are not significantly different at $P<0.05$.

Table 4. Correlation analysis between soil chemical and electrochemical properties

	pH	EC	CEC	φ_0	σ_0	E_0	SSA
EC	0.595*						
CEC	0.551*	0.317					
φ_0	0.883**	0.701**	0.737**				
σ_0	0.683**	0.420	0.716**	0.775**			
E_0	0.764**	0.496	0.901**	0.875**	0.880**		
SSA	0.442	0.264	0.984**	0.666**	0.634*	0.842**	
SCN	0.515*	0.320	0.997**	0.718**	0.708**	0.896**	0.989**

Note: **, significant at $p<0.01$; *, significant at $p<0.05$.

Table 5. Relationship between soil basic physicochemical properties and the surface electrochemical properties.

	SOM (g/kg)	Bulk density (g/cm^3)	Porosity (%)	Clay (%)	Sand (%)	Silt (%)
pH	0.489	-0.379	0.379	0.830**	-0.764**	0.307
EC (dS/cm)	0.150	-0.149	0.149	0.706**	-0.754**	0.447
CEC (cmol/kg)	0.960**	-0.733**	0.734**	0.564*	-0.356	0.316
SSA (m^2/g)	0.937**	-0.712**	0.712**	0.592*	-0.436	0.269
φ0 (mv)	0.658**	-0.537*	0.537*	0.877**	-0.857**	0.413
σ0 (cm^{-2})	0.659**	-0.355	0.355	0.497	-0.571*	0.389
E0 (Vm^{-1})	0.823**	-0.531*	0.532*	0.565*	-0.637*	0.419
SCN (cmol/kg)	0.944**	-0.702**	0.703**	0.534*	-0.417	0.329

Note: **, significant at $p<0.01$; *, significant at $p<0.05$.

study were all positively correlated with each other as shown in Table 4. However, EC had no significant correlations with CEC, σ_0, E_0, SSA, and SCN while pH had no significant correlations with SSA. There were significant positive correlations between CEC and φ_0 ($r = 0.737$), σ_0 ($r = 0.716$), E_0 ($r = 0.901$), SSA ($r = 984$), and SCN ($p<0.01$). SSA was significantly positively correlated with σ_0 ($r = 634$, $p<0.05$) while the surface charge characteristics were all significantly positively correlated with each other ($p<0.01$). The increased organic matter contents with the application of the organic materials could be the main reason for this observation. Again, the significant linear relationship between CEC and SSA may be due to the high specific surface area of organic matter which forms the greatest component of soil organic carbon thereby improving the substitution sites for cation exchange in the soil [6]. The relationship between soil basic physicochemical properties and the surface electrochemical properties is shown in Table 5. The SOM was highly significantly positively correlated with all the surface electrochemical properties ($P<0.01$) except pH and EC, which were positively correlated with SOM but not significant. Bulk density and sand were negatively correlated with all the surface electrochemical properties whiles the percentage of clay, silt, and porosity were positively correlated with all the surface electrochemical properties. Among the particle size distribution, clay had highly significant positive correlations with pH, EC, and surface potential ($P<0.01$) while it also had significant positive correlations with CEC, SSA, electric field strength, and SCN ($P<0.01$) indicating that clay forms an important granulometric property that affects the surface electrochemical properties of soil. Soil properties such as EC soil texture, cation exchange capacity (CEC), drainage conditions, organic matter level, and subsoil characteristics correlate with each other and affect crop productivity [9]. Similar findings were recorded in this study which can be mainly attributed to the significant correlations and relations between these properties as Fungo et al. [55] and Kumar et al. [56] reported that the basic cations, CEC, and pH had strong positive relations with each other in their studies. Liu et al. [6] also reported that CEC, SSA, and soil organic matter were significantly correlated with each other, thereby improving the substitution sites for cation in the soil.

Conclusion

The application of organic materials can positively improve the chemical and electrochemical properties of soil compared with the control (CK). Moreover, the different organic matter sources had different effects on the studied properties which indicates that in improving soil qualities with organic fertilization, specific soil properties can be amended by specific organic amendments. In this study, the long-term application of organic materials improved the soil electrochemical properties where the highest pH and EC were recorded in chicken manure (JM) and cow manure (CM) treatments respectively. The highest cation exchange capacity (CEC) and specific surface area (SSA), were recorded in treatment tree leaves treatment (TL). The surface charge characteristics were significantly positively correlated with each other and the soil physicochemical properties suggesting that the granulometric properties, organic materials, and other physical attributes form part of the factors that affect the soil chemical and electrochemical properties. The application of the organic materials on the surface affected the soil properties in the subsurface layer however did not result in a significant increase in sub-layer soil properties compared to the surface attributes. In all treatments, TL is highly recommended since it had a more advantageous effect on enhancing the surface charge characteristics and physicochemical attributes of the soil. Soil chemical and electrochemical properties play important roles in improving soil quality hence improving these attributes with the application of organic materials are imperative. Therefore it is important to put forward some strategies for the management, treatment, and application of different organic wastes in farmlands as they greatly enhance the fertility and productivity indicators of soil. This will present strategies for improving soil quality and increasing arable land resources.

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Conflict of Interest

The authors declare no conflict of interest.

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