Effects of Returning Organic Fertilizer and Biochar to Soil on Surface Electrochemical Properties and Nutrients

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The soil application of organic materials, such as biochar and organic fertilizers, serves as an important approach to maintaining soil nutrient cycling and enhancing soil quality. Here the effects of biochar and organic fertilizer application were comparatively analyzed relative to soil organic matter, NPK (nitrogen, phosphorus, potassium) content, and soil surface electrochemical properties. The primary factors influencing soil surface electrochemical properties were identified. It was found that application of two organic materials could increase the contents of total nutrients and available nutrients. Among all indicators, nitrate nitrogen showed the most significant increase, with T1 and T2 increasing by 34.2% and 75.7% compared to CK, respectively. The two organic materials enhanced soil surface charge quantity, specific surface area, and surface charge density. SOC and HS contents were identified as the top two influencing factors for changes in soil surface electrochemical properties. The explanation index of SOC reached 70.1% and 39.4% for T1 and T2, while those of HS were 20.3% and 31.2%, respectively. These efforts elucidated the impacts of the return of organic fertilizer and biochar to the field on soil surface electrochemical properties, which could provide data support for enhancing arable land quality and fostering healthy soil development.

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Keywords: Organic fertilizer; Biochar; Soil surface electrochemical properties; Nutrients

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INTRODUCTION

Soil is an essential component of terrestrial ecosystems and serves as the medium for numerous ecological processes (Chen *et al*. 2020). Soil in nature typically carries both positive and negative charges simultaneously, and in most cases, the number of negative charges exceeds that of positive charges, so soils generally carry a net negative charge. The charges in soil are primarily provided by soil colloids, which refer to soil particles with diameters ranging from 1 to 1000 nm. These colloids serve as the main sites for various chemical and biochemical processes in soil (Xu *et al*. 2018). They represent the finest and most active components within the soil matrix (Lekfeldt *et al*. 2017). Soil surface electrochemical properties, with surface potential, charge quantity, specific surface area, electric field strength, and charge density as the main parameters, are important physical and chemical properties of soil. By influencing the adsorption and desorption of ions, migration and transformation of elements, and hydraulic properties in soil, among others, they profoundly affect issues such as soil nutrient retention, crop growth, soil erosion, and non-point source pollution (Hu *et al*. 2018). Besides being influenced by external factors such as climate and vegetation, the main internal influencing factors of soil surface electrochemical properties include soil mineral composition, organic matter content, pH value, and so on (Liu *et al*. 2020; Tu *et al*. 2022). Liu *et al*. (2020) found in their study on degraded grassland ecosystems that the restoration of soil fertility was accompanied by an increase in soil cation exchange capacity and specific surface area, as well as a decrease in surface potential. Lee *et al*. (2019) revealed through a study on columnar sandy soil that, influenced by electrochemical properties, Ca^{2+} had a more significant retention effect on colloids than Na^{+}, and soil colloids could also inhibit the migration of ammonia nitrogen.

Agricultural organic residue is an inevitable byproduct of the agricultural production process, and fertilizer-based utilization is the most important technical route for its resource utilization (Li *et al*. 2023). The return of organic materials to fields can effectively increase soil organic matter and nitrogen, phosphorus, and potassium nutrients, improve soil quality, and enhance agricultural product quality. Meanwhile, through the interaction between their own components and soil particles, organic materials affect soil surface electrochemical properties in terms of material input, interface reactions, and environmental regulation, among other aspects. For instance, organic materials contain a large number of organic colloids (such as humic acid, fulvic acid, and cellulose derivatives), which themselves carry abundant variable charges and can increase the total soil charge amount and regulate charge density (Wen *et al*. 2024).

There are various types of agricultural residues, and the methods of utilization as fertilizer differ. Aerobic composting to produce organic fertilizer and high-temperature carbonization to produce biochar are the most commonly used fertilizer-based treatment methods. Existing studies have shown that biochar application to fields could increase nutrient content, pH value, porosity, and organic matter in soil to varying degrees, while reducing soil bulk density and the bioavailability of heavy metals (Jin *et al*. 2024). Biochar significantly increased the specific surface area of soil, enhanced the soil's adsorption capacity, thereby improving the soil's field water-holding capacity, which in turn increased the available water content in the soil that is available for crop use (Seyedsadr *et al*. 2022). Arwenyo *et al*. (2023) reported that biochar application can increase soil cation exchange capacity; however, other studies indicated that the addition of biochar had no significant effect on the cation exchange capacity of soil (Chen *et al*. 2013). The differences may stem from the differences in the physical and chemical properties of the soil. Huang *et al*. (2022) found that organic fertilizer improves the stability of soil structure, promotes the soil clayization process, and reduce the loss of silty clay particles. The enrichment of silty clay particles increased the surface charge amount and specific surface area of the soil. Moreover, organic fertilizer could increase the content of soil organic matter, which itself carried a large number of variable charges and could effectively modify the soil surface electrochemical properties (Xie *et al*. 2024). Wang *et al*. (2021) found that, in comparison with chemical fertilizers, organic fertilizers led to a greater improvement in soil surface electrochemical properties, with parameters such as soil surface charge, surface charge density, and electric field strength increasing to varying degrees. Consequently, this enhanced the retention rate of ammonia nitrogen and lowered the risk of its loss. The physical attributes of organic fertilizers, particularly their granulometric properties, play a crucial role in modifying the soil's chemical and electrochemical state. This modification is characterized by a strong positive correlation among various soil surface charge parameters and with the overall chemical properties. Therefore, applying organic fertilizers to enhance soil surface electrochemistry is a feasible strategy for improving agricultural soil quality (Opoku-Kwanowaa *et al.* 2022).

As soil surface electrochemical regulators, organic fertilizer and biochar differ distinctly. Organic fertilizers, *via* microbial decomposition, release organic acids and soluble organics, dynamically altering soil surface charge density. Electrolytes present in the organic matter reduce the electrical double layer thickness, though the resulting regulation of surface potential is short-lived (Wang *et al*. 2021). Biochar, however, which has a stable porous structure and oxygen-containing functional groups, stably elevates negative surface potential and reduces electric field strength, offering long-lasting effects (Qiao *et al*. 2018). These differences arise from their properties: organic fertilizer contain labile organic matter, whose decomposition drives transient electrochemical changes, while biochar's pyrolysis-derived stable structure and persistent functional groups enable sustained, steady modulation of soil electrochemical environments.

Although there have been many studies on the effects of organic fertilizer and biochar application on soil properties and functions at present, these studies mainly focus on aspects such as soil organic carbon and nutrient element cycling (Cao *et al*. 2025), aggregate stability (Yu *et al*. 2017), water infiltration (Wang *et al*. 2022), and microbial functions (Zhou *et al*. 2024). However, there is still a lack of systematic research on how soil surface electrochemical properties change, and the correlation between basic physicochemical properties of soil and surface electrochemical property parameters is not clear. Therefore, this study conducted an in-depth comparative study on the effects of organic fertilizer and biochar application on soil surface electrochemical properties and nutrients, and identified the main factors affecting the changes of soil surface electrochemical properties in this process through redundancy analysis. This study provides a scientific basis for in-depth understanding of the mechanisms of soil improvement by organic fertilizer and biochar application.

EXPERIMENTAL

The experimental site is located in a family farm in Jurong City, Jiangsu Province, China (119°8'N, 31°54'E). This area is in the north subtropical monsoon climate zone, with four distinct seasons. The annual average temperature is 15.1 °C, the extreme maximum temperature is 39.2 °C, and the extreme minimum temperature is -14.8 °C. The average annual sunshine duration is 2116 h, the annual average relative humidity is 78%, and the monthly rainfall data after the start of the experiment is shown in Fig 1. The area selected for the experiment is the basic farmland of the park, with the following soil properties: soil organic matter content of 22.3 g/kg, total nitrogen content of 0.146%, total phosphorus content of 0.75 g/kg, total potassium content of 15.4 g/kg, available phosphorus content of 58.8 mg/kg, available potassium content of 301 mg/kg, nitrate nitrogen content of 72.6 mg/kg, and pH value of 7.6. The experiment was conducted in April 2023, with a total of 3 treatments: the blank group with no fertilizer added, denoted as CK; the T1 group with biochar application; and the T2 group with organic fertilizer application. The application rates of the two types of organic materials were both 7.5 t/ha. Biochar was purchased from a company in Nanjing, using rice straw as its main raw material. Organic fertilizer was purchased from an organic fertilizer factory in Nanjing, with tomato straw and livestock and poultry manure as its main raw materials. And it was produced using a trough aerobic composting process with a duration of 45 days, meeting the requirements of the NY525-2021 standard for organic fertilizers in China. The main physical and chemical parameters of the selected organic materials are shown in Table 1.

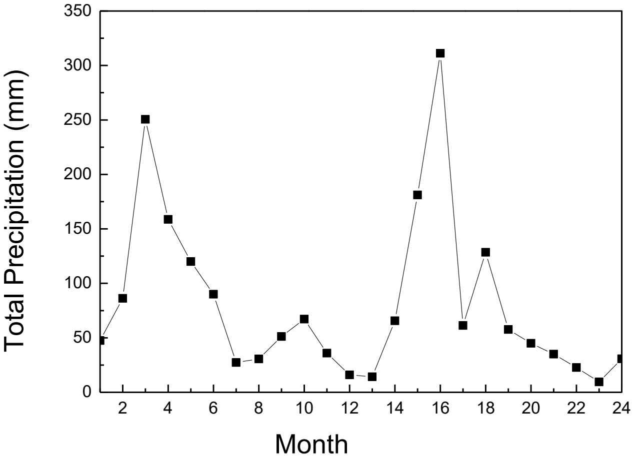

Fig. 1. Monthly precipitation at the experimental site

Table 1. Physicochemical Properties of Two Organic Materials

Parameters	SOC (%)	TN (%)	TK (%)	TP (%)	pH
organic fertilizers	23.15 ± 1.14	1.58 ± 0.09	3.69 ± 0.17	1.45 ± 0.07	7.44 ± 0.26
Biochar	31.91 ± 1.27	1.01 ± 0.12	1.55 ± 0.11	0.43 ± 0.04	8.39 ± 0.29
SOC: Soil Organic Carbon; TN: total nitrogen; TK: total potassium; TP: total phosphorus					

Determination of Physical and Chemical Properties of Soil

Soil samples were collected by setting sampling points using the S-shaped 5-point method in each plot. At each sampling point, soil profile samples were taken from three layers: 0-10 cm, 10-20 cm, and 20-30 cm. A total of approximately 500 g of mixed soil samples were collected. Stones and animal/plant residues in the collected soil were manually removed; the soil was then ground, sieved, and packed into bags for later use in soil chemical analysis.

The total organic carbon content in soil was determined by the method of potassium dichromate oxidation-ferrous sulfate titration. The total nitrogen content in soil was determined using a Kjeldahl nitrogen analyzer (KDY-9830, China). Ammonium nitrogen and nitrate nitrogen were determined using a flow analyzer (iFIA7, China). Quantification of total potassium employed flame photometry, while total phosphorus was analyzed *via* the spectrophotometric method of alkali fusion-Mo-Sb Anti. The extraction of available phosphorus was performed using 0.5 mol/L sodium bicarbonate solution, followed by quantification via the Mo-Sb Anti colorimetric method. Available potassium was extracted with 1 mol/L ammonium acetate solution and subsequently analyzed by flame photometry; pH was determined by the electrode method, with a soil-to-water ratio of 2.5. For zeta potential analysis (Xu *et al.* 2012), 0.05 g of soil sample (sieved through a 300 mm mesh) was placed in a 250 mL conical flask with 200 mL of deionized water. The mixture was ultrasonically dispersed for 1 h. The resulting suspension was then aliquoted into 6 equal portions and allowed to stand for 2 days. Zeta potential was subsequently measured using a Zeta Potential Analyzer (PALS, Brookhaven Instruments, USA).

Determination of Electrochemical Properties of the Soil Surface

Li *et al*. (2011) conducted a detailed study on the measurement of soil surface electrochemical properties. In their research, two modifications were initially introduced: one for the nonlinear Poisson-Boltzmann equation and another for the cation exchange equilibrium equation. Subsequently, new equations for describing cation exchange equilibrium, which account for the cationic hydration effect, were derived from the modified Poisson-Boltzmann equation. Ultimately, a theoretical framework was established to enable the combined determination of five surface properties from a single cation exchange equilibrium experiment. Using the combined determination method for material surface properties proposed by Li, the soil surface electrochemical properties were measured, as follows:

1. Decalcification treatment: Soil samples were first sieved through a 0.25 mm mesh, subsequently immersed in 0.5 mol/L HCl solution with agitation, and finally subjected to repeated washing until cessation of visible bubble formation.
2. Preparation of hydrogen-saturated soil samples: Stir the decalcified soil repeatedly with a 0.1 mol/L HCl solution, then remove the supernatant. After repeating this process 3 times, use deionized water of the same volume to shake repeatedly to remove Cl^- from the suspension. Centrifuge to remove the supernatant, then dry the obtained soil sample at 65 °C. After grinding and passing through a 0.25 mm sieve, pack it into a bag for later use.
3. Determination of ion exchange adsorption: Weigh 5 to 10 g of hydrogen-saturated soil sample, add 40 mL of a mixed solution of 0.0075 mol/L NaOH and $Ca(OH)_2$, and shake for 24 hours. Then add 1 mol/L HCl solution dropwise to adjust the pH of the mixed solution to 7. After centrifuging to obtain the supernatant, determine the concentrations of Ca^{2+} and Na^+ in the supernatant using a flame photometer and an atomic absorption spectrophotometer, respectively. Three replicates were set for each soil sample.

The electrochemical properties were calculated as follows,

Surface potential φ_0 (mV):

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

Surface charge density σ_0 (c/m^2)

$$\sigma_0 = sgn(\varphi_0)\sqrt{\frac{\varepsilon RT}{2\pi}\left(a_{Na}^0 e^{\frac{\beta_{Na}F\varphi_0}{RT}}\right) + a_{Ca}^0 e^{\frac{2\beta_{Ca}F\varphi_0}{RT}}} \tag{2}$$

Surface electric field intensity E_0 (V/m)

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

Specific surface area S (m^2/g)

$$S = \frac{N_{Na}k}{\mathrm{m}a_{Na}^0} e^{\frac{\beta_{Na}F\varphi_0}{2RT}} = \frac{N_{Ca}k}{\mathrm{m}a_{Ca}^0} e^{\frac{\beta_{Ca}F\varphi_0}{RT}} \tag{4}$$

$$k = \sqrt{\frac{8\pi F^2 C_0}{\varepsilon RT}} \tag{5}$$

$$m = 0.5259\ln\left(\frac{c_{Na}^0}{c_{ca}^0}\right) + 1.992 \tag{6}$$

Surface charge number *SCN* (coml/kg)

$$SCN = 10^5 \frac{S\sigma_0}{F} \tag{7}$$

where a_{Na}^0 (mol/L) and a_{Ca}^0 (mol/L) represent the activities of Na^+ and Ca^{2+} in the solution, respectively; N_{Na} (mol/g) and N_{Ca} (mol/g) represent the adsorption capacities of Na^+ and Ca^{2+} in the soil, respectively; T represents the absolute temperature, and T=298 K; R (J/K mol) represents the universal gas constant; F (C/mol) represents the Faraday constant, and F=9.6485×10^4 C/mol; β_{Ca} and β_{Na} represent the effective charge coefficients of Ca^{2+} and Na^+, respectively. ε represents the dielectric constant of water, and ε equals 8.9×10^{-9}(C^2/J m); k represents the Debye parameter.

Data and Statistical Analyses

Data processing was carried out with Excel 2016, while statistical evaluations were performed using SPSS 22.0. Graphical representations were generated in Origin 2022. Analysis of variance (ANOVA) was implemented through Statistical Analysis System (SAS) version 9.4. Mean values were compared adopting Tukey's honest significant difference test at a 0.05 significance threshold. Redundancy analysis (RDA) was conducted using Canoco 5.0.

RESULTS AND DISCUSSION

Changes in Soil Nutrients

The effects of applying organic fertilizers and biochar on soil nutrients are shown in Table 2. Benefiting from the relatively high content of nutrient elements in biochar and organic fertilizers (Sarangi *et al*. 2021), varying degrees of increase were observed in the content of most soil nutrient elements. The changes in the contents of total nutrients and total available nutrients in the soil are shown in Fig. 2. Compared to CK treatment, T1 and T2 increased the total nutrient content of soil by 1.36% and 7.74%, respectively, while the total available nutrients increased by 22.56% and 51.26%, respectively (Fig. 2). This indicated that the effect of applying biochar and organic fertilizers on increasing available nutrients (which can be directly used by plants) in the soil was significantly better than the increase in total nutrients.

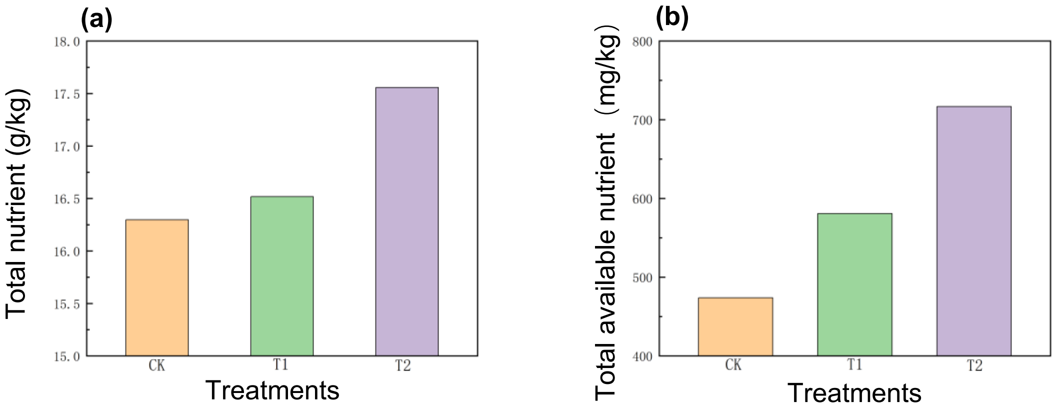

Fig. 2. The contents of total nutrients (a) and total available nutrients (b) in the soil (CK: no fertilizer added; T1: biochar application; T2: organic fertilizer application)

Table 2. Nutrient Content in Soil under Three Treatments

Parameters	CK	T1	T2
TN (g/kg)	1.46 ± 0.07	1.48 ± 0.04	1.67 ± 0.09
TP (g/kg)	0.75 ± 0.02	0.77 ± 0.04	0.99 ± 0.04
TK (g/kg)	15.41 ± 0.43	15.63 ± 0.39	16.42 ± 0.52
AP (g/kg)	58.73 ± 3.07	59.57 ± 4.25	96.61 ± 7.51
AK (g/kg)	300.26 ± 24.66	380.75 ± 31.07	460.49 ± 46.98
NH_4^+-N (g/kg)	42.64 ± 2.15	43.91 ± 1.98	32.77 ± 1.42
NO_3^--N (g/kg)	72.55 ± 5.31	97.35 ± 6.25	127.45 ± 9.84
AP: available phosphorus; AK: available potassium			

Regarding individual nutrients, the largest increase was observed in nitrate nitrogen, with T1 and T2 treatments showing increases of 34.2% and 75.7% compared to CK, respectively, and available potassium also increased by 26.7% and 53.3%, respectively (Table 2). Among all indicators, a 23.2% reduction in ammonium nitrogen content was recorded for T2 treatment (*vs*. CK), representing the only decrease under all treatments. This was mainly because the vast majority of ammonium nitrogen in the organic fertilizer had been converted to nitrate nitrogen. Moreover, the organic fertilizer contained a large number of microorganisms and nutrients, which stimulated the activity of soil microorganisms and promoted the conversion of ammonium nitrogen to nitrate nitrogen in soil (Zhang *et al*. 2018). That was also an important reason for the increase in nitrate nitrogen content in the T2 treatment. As nitrate is more prone to leaching losses, to better conserve nitrogen, nitrification inhibitors could be applied concurrently with organic fertilizer to minimize nitrogen loss.

Changes in Soil Organic Carbon and Humus

The effects of applying organic fertilizers and biochar on soil organic carbon and humus are shown in Fig. 3. Similar to the effects on changes in soil nutrient content, there was a benefit from the input of relatively high organic matter content in biochar and organic fertilizers (Wang *et al*. 2024). The soil organic carbon content increased in both of the treatments. Thus, T1 and T2 treatments increased the value by 25.1% and 8.5%, respectively, compared with CK. The effect of applying biochar on increasing soil organic carbon in the soil was significantly better than that of applying organic fertilizers($p < 0.05$). The difference among these was mainly attributed to the fact that the organic matter content in biochar was higher than that in organic fertilizers. However, as shown in Fig. 3b, the effects of the two organic materials on soil humus content exhibited a different trend compared to their effects on soil organic matter content. The increase in soil humus in the T1 treatment was only 6.12%, far lower than the 42.31% increase observed in the T2 treatment. This was primarily attributed to the fact that the biochar was formed through a chemical pyrolysis process, resulting in a core structure of highly aromatic and stable carbon skeletons. It contained a small amount of residual lignin, cellulose fragments, and surface functional groups (such as hydroxyl groups and carboxyl groups). However, it predominantly constituted an inert or semi-inert carbon. During the pyrolysis process, the easily decomposable organic matter (such as polysaccharides and proteins) in biomass had been largely destroyed, and thus could not form humus (Cao *et al*. 2024). Its raising effect of humus in the soil was mainly attributed to its favorable pore structure and physicochemical properties, which could indirectly promote the formation of humus in the soil (Cao *et al*. 2025). By contrast, organic fertilizer was formed *via* biochemical processes, where microorganisms (bacteria, fungi) converted raw organic matter into stable humus through mineralization and humification. Since it inherently contained substantial humus (Zhang *et al*. 2023), organic fertilizer could directly boost soil humus content. Moreover, the numerous microorganisms it carried also promoted the formation of new humus in the soil (Li *et al*. 2025).

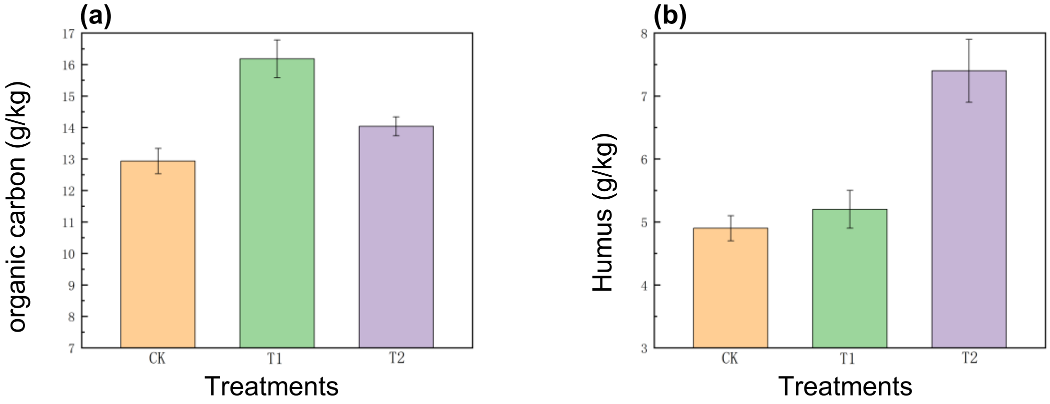

Fig. 3. The contents of organic carbon (a) and humus (b) in the soil

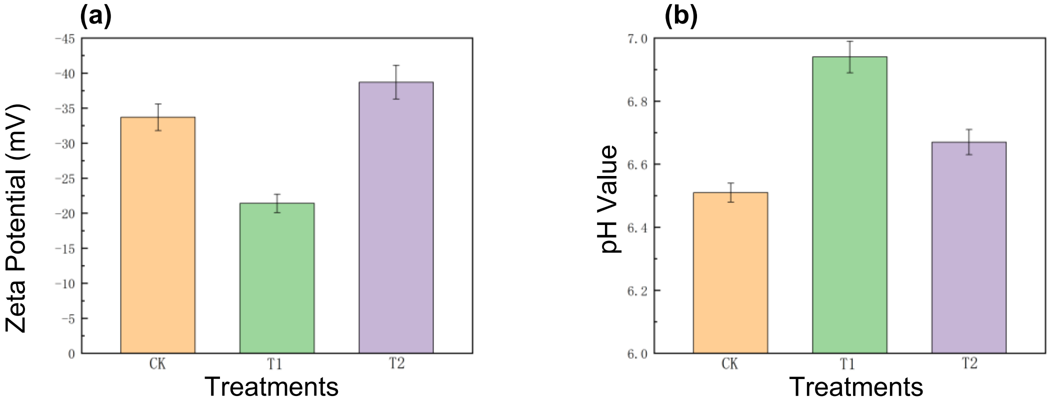

Fig. 4. Changes in the soil colloidal zeta potential (a) and pH (b)

Changes in the Soil Colloidal Zeta Potential and pH

The effects of applying organic fertilizers and biochar on soil colloidal zeta potential and pH value are shown in Fig. 4. The application of two types of organic materials increased soil pH. This was mainly attributed to the high pH values of biochar and organic fertilizers themselves. The pH values reached 8.4 and 7.4, respectively, both higher than the original soil pH value (Table 1). Additionally, the HCO_3^- and organic anions released during the decomposition of organic fertilizers could also slightly increase the soil pH value. The soil colloidal zeta potential refers to the potential difference between the surface of the particles and the bulk of the surrounding solution. It is a key parameter that reflects the charged state of the soil colloids and the interactions between particles, influencing the soil's adsorption and migration of nutrients. The zeta potential of CK soil colloids was -33.7 mV, indicating a predominantly negative surface charge. Biochar application was able to significantly raise the zeta potential to -21.4 mV ($P < 0.05$), with the absolute value decreasing by 36.5%. Conversely, organic fertilizer application could significantly lower it to -38.7 mV ($P < 0.05$), with the absolute value increasing by 14.8%.

The opposite regulatory directions of the two organic materials on zeta potential indicated fundamental differences in their interfacial interaction mechanisms with soil colloids. The biochar was rich in aromatic structures and alkaline functional groups (such as phenolic hydroxyl groups) on its surface. In the soil solution, it formed positively charged regions under protonation, neutralizing the negative charges on the colloid surface. Concurrently, the cations such as Ca^{2+} and K^+ released by biochar compressed the electrical double layer, reducing the absolute value of the zeta potential (Tu *et al.* 2022). However, the humus produced by the decomposition of organic fertilizers contained a large number of carboxyl groups and phenolic hydroxyl groups. Under neutral conditions, the carboxyl groups dissociated and released H^+, forming negatively charged carboxylate ions and increasing negative charges. Additionally, soluble organic matter was adsorbed on the colloid surface, with its carboxyl groups further contributing negative charges, ultimately resulting in a more negative zeta potential (Wen *et al.* 2024).

Changes in Soil Surface Electrochemical Properties

The effects of applying organic fertilizers and biochar on the soil surface electrochemical properties are shown in Table 3. The application of these two organic materials effectively increased the soil surface charge number and specific surface area. For the T1 and T2 treatments, the soil surface charge number and specific surface area reached 20.0 cmol/kg and 58.7 m²/g, and 17.2 cmol/kg and 41.6 m²/g, respectively. Compared with CK, these values were 66.7% and 43.3% higher for T1, and 72.1% and 21.5% higher for T2. This was mainly because both the humus in organic fertilizers and biochar itself had high surface charge number and specific surface area, which directly increased the relevant parameters of the soil. This conclusion was consistent with the research conclusions of Yang *et al*. (2023). Owing to isomorphous substitution and functional group dissociation, soil colloids possessed a net negative charge, leading to the soil surface potential generally exhibiting negative values. After the application of biochar, the soil surface potential increased from -101.4 to -98.7 mV (with a decrease in absolute value), and the surface electric field strength decreased from 3.01×10^8 to 2.33×10^8 V/m. These changes were attributed to the protonation of alkaline functional groups on biochar surfaces, thereby neutralizing negative charges, along with released cations compressing the electrical double layer. Moreover, biochar dispersed localized charge concentrations and diminished local charge density within the soil matrix. Concurrently, its enhancement of soil porosity forced apart charged soil particles previously in close contact, leading to a weakening of the soil electric field (Tu *et al.* 2022). However, organic fertilizer application caused the soil surface potential to decrease from -101.4 to -109.1 mV (with an increase in absolute value), while the surface electric field strength increased to 5.25×10^8 V/m. Because the humus produced by the decomposition of organic fertilizer contained a large number of dissociable functional groups (carboxyl groups, phenolic hydroxyl groups), it released negative charges after deprotonation, which strengthened the surface electric field intensity and negativity of surface potential, and thus better facilitated the adsorption of cationic nutrients (Ding *et al.* 2017). In contrast, an enhanced soil surface electric field strength within a certain range increased the adsorption and retention capacity for cationic nutrient ions (such as NH_4^+, K^+, Ca^{2+}, and Mg^{2+}). This effectively reduced the leaching loss of these valuable nutrients and improved the soil's nutrient retention capacity. Tu *et al.* (2022) reported that lower biochar application rates (1 to 5%) decreased soil surface potential (increasing absolute values), while higher rates (7 to 10%) produced effects consistent with the findings. This might have been primarily because low-dose biochar mainly functioned as a negative charge supplement in the soil, thereby reinforcing the negative charge dominance of soil colloids. However, as the proportion of biochar in the soil increased, the original negative charge supplementation mechanism weakened, giving way to a negative charge saturation and positive charge competition dominated reversal of charge balance.

Table 3. Changes in Soil Surface Electrochemical Properties under Three Treatments

Treatment	SCN (cmol/kg)	*S* (m²/g)	σ_0 (c/m²)	φ_0 (mV)	E_0 (10^8V/m)
CK	11.97 ± 0.06a	34.12 ± 1.95a	0.35 ± 0.03a	-101.39 ± 2.44a	3.01 ± 0.23a
T1	19.95 ± 0.13c	58.73 ± 2.65c	0.34 ± 0.02a	-98.68 ± 2.27a	2.33 ± 0.25b
T2	17.15 ± 0.09b	41.46 ± 1.37b	0.41 ± 0.01b	-109.06 ± 2.14b	5.25 ± 0.17c

SCN: Surface charge number; *S*: Specific surface area; σ_0: Surface charge density; φ_0: Surface potential; E_0; Surface electric field intensity. Statistically significant differences ($p \leq 0.05$) among the treatments, as determined by a Tukey's honest significant difference test, are indicated by different letters.

Influence of Physicochemical Properties on Soil Surface Electrochemical Properties

The influence of physicochemical properties on soil surface electrochemical properties is shown in Fig. 5. The surface charge number (SCN), specific surface area (*S*), surface charge density (σ_0), surface potential (φ_0), and surface electric field intensity (E_0) were used as response variables, while six soil physicochemical properties-soil organic carbon (SOC), humic substances (HS), pH, total nitrogen (TN), total phosphorus (TP), and total potassium (TK) served as explanatory variables for redundancy analysis ordination. It was observed that for the treatments with biochar addition, the explanation index of the basic physicochemical properties of soil on the first axis and the second axis was 92.37% and 7.51%, respectively, reaching a cumulative explanation index of 99.88%. For the treatments with organic fertilizer addition, the explanation index of the physicochemical properties of soil on the first axis and the second axis was 91.81% and 6.71%, respectively, reaching a cumulative explanation index of 98.52%. Fig. 5c showed that for the T1 treatment, the importance ranking of soil basic physicochemical property indicators was SOC > HS > PH > TN > TP, with the explanation index of SOC reaching 70.1%, significantly higher than other indicators ($p < 0.05$). For the T2 treatment (Fig. 5d), the order of importance of the indicators of soil's physicochemical properties was SOC > HS > TN > pH > TK. Among these indicators, the explanation index of SOC was the highest at 39.4%, followed in sequence by 31.2% for HS and 25.7% for TN. Overall, SOC was the dominant factor affecting soil surface electrochemical properties in both treatments. High surface charge density and cation adsorption sites of organic carbon could increase the quantity of soil surface charges. Furthermore, organic carbon could also enhance the formation of organo-mineral complexes, thus further increasing the quantity of soil surface charges. Additionally, after biochar and organic fertilizer were applied to the soil, the functional groups in organic carbon underwent changes: active groups such as carboxyl groups, hydroxyl groups, and aldehyde groups increased (Sheng *et al.* 2020), and these groups could dissociate to release H^+, thereby causing an increase in the negative charges on the soil surface. Studies by Hu *et al.* (2021) further found that with the increase of soil organic carbon, the surface charge characteristics of soil particles altered, causing a significant increase in the molecular attraction between soil particles, thereby enhancing the stability of soil aggregates.

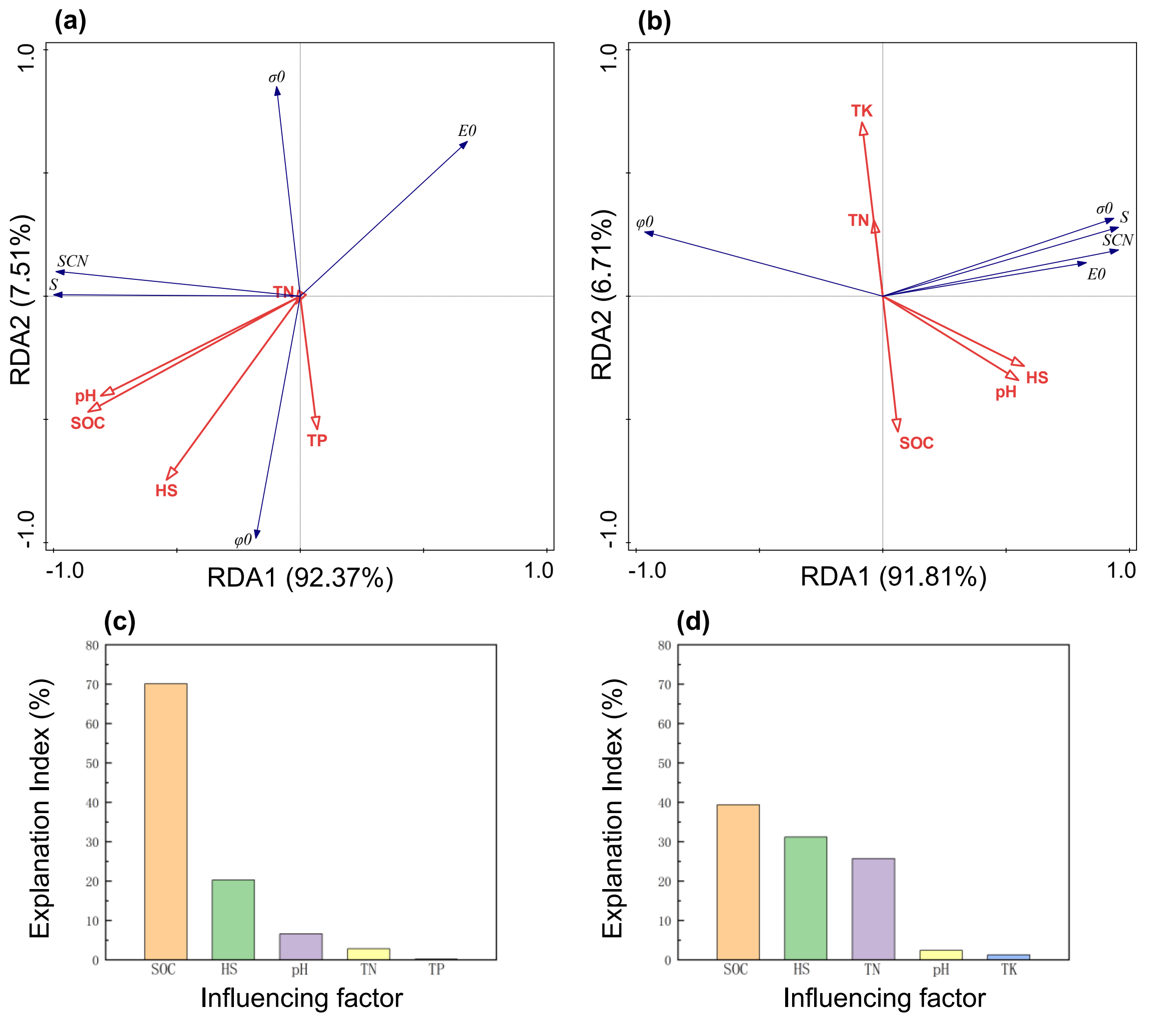

Fig. 5. Redundancy analyses (RDA) between physicochemical properties and soil surface electrochemical properties. (a) Redundancy analyses figure for T1; (b) redundancy analyses figure for T2. (c) Explanation of influencing factors for T1; (d) explanation of influencing factors for T2

CONCLUSIONS

1. The application of organic fertilizer and biochar were both able to increase the contents of total nutrients and available nutrients in the soil, and the increase in available nutrients was significantly higher than that in total nutrients ($p < 0.05$). Among all indicators, nitrate nitrogen exhibited the most significant increase, with T1 and T2 treatments showing increases of 34.2% and 75.7% respectively compared to the control (CK) treatment. It is worth noting that the application of organic fertilizer might reduce the content of ammonium nitrogen in the soil, but the contents of total nitrogen and nitrate nitrogen still increased.
2. The application of organic fertilizer and biochar enhanced the amount of soil surface charge, specific surface area, and surface charge density, while biochar reduced the surface electric field intensity and absolute value of surface potential. From the RDA analysis, it could be concluded that the contents of SOC and HS in the soil were both

the main influencing factors for the changes in soil surface electrochemical properties in the two treatments. In the T1 treatment, the explanation index of SOC reached 70.1%, and that of HS was 20.3%; in the T2 treatment, the explanation index of SOC was 39.4%, and that of HS was 31.2%.

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