

Original Research

Soil Surface Electrochemical Properties in a Karst Ecosystem and Its Response to Rocky Desertification Evolution, SW China

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Abstract

Rocky desertification control is an effective way to reconstruct degraded ecosystems and restore soil function in karst areas. Soil surface electrochemical properties, including soil surface potential, surface charge density, surface electric field strength, specific surface area, and surface charge number are important indicators for evaluating agricultural soil quality and environmental carrying capacity. However, little attention has been paid to the effect of rocky desertification succession on soil electrochemical properties. In this study, we selected a sequence of rocky desertification succession (nil, slight, moderate, and severe) to study the changes in soil surface electrochemical properties during the succession of rocky desertification. Our results showed that with increasing rocky desertification intensity, soil surface charge density, surface charge intensity, specific surface area, and the numbers of surface charge decreased, while the soil surface potential increases. The results showed that humus composition, soil particle size composition, and metal oxide content were important environmental factors that determine the electrochemical properties of soil surface in a karst rocky desertification area. In terms of impact on surface charge properties, soil properties displayed an order of humus>particle size composition>metal oxides. In addition, through the comparative analysis of soil physical properties and surface electrochemical properties, it was found that the surface soil aggregates of severe rocky desertification were more likely to disintegrate when precipitation occurs, thus facing a higher risk of soil erosion. Our results showed that the electrochemical properties of soil surface decrease with the increase of rocky desertification grades, which contributed to the decline of soil water and fertilizer

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conservation capacity. Therefore, areas under severe rocky desertification should be put under priority control.

Keywords: karst, soil surface electrochemical, rocky desertification, soil physical and chemical properties, evolution

Introduction

Karst landforms are formed by the dissolution of carbonate rocks by surface water and groundwater [1]. Guizhou, as a representative of the Southwest China karst region, is the center of the East Asia karst development area, which is one of the three concentrated contiguous karst regions in the world [2]. Due to the low environmental carrying capacity and prominent contradiction between plowland and humans, a series of ecological degradation phenomena of rocky desertification, such as vegetation destruction, soil erosion, and bedrock exposure, are particularly common in this region [3-4]. With the continuous development of the degradation intensity of rocky desertification, soil erosion is intensified, and the capacity of soil to store, maintain, and supply fertilizer rapidly decreases until there is a loss of land productivity [5-6]. Karst rocky desertification has become a major ecological problem restricting agricultural production and social and economic development in Southwest China [7]. Rocky desertification control is not only an important strategy for China's national ecological protection and construction, but is also urgently needed for local social and economic sustainable development [8]. However, for a long time, the lack of in-depth understanding of soil quality response laws and the internal driving mechanism in the process of karst rocky desertification succession has seriously restricted the effectiveness of rocky desertification control [9].

Soil is an important part of terrestrial ecosystems, is the location of many ecological processes in the ecosystem, and is an indispensable research subject in the study of plant community regeneration and succession processes [10-11]. Soil colloids refer to soil particles with a diameter of 1-1000 nm, which are the main sites for various chemical and biochemical processes in soil [12]. Soil colloids concentrate most of the negative charges in the soil, and, therefore, are the most subtle and active soil component [13]. The surface potential, surface charge number, surface electric field strength, specific surface area, and surface charge density of soil colloids have profound impacts on a series of physical and chemical processes such as adsorption and desorption of ions and molecules, occurrence and migration of nutrient elements, and hydraulic characteristics [14-16]. Liu et al. found that the restoration of soil fertility was accompanied by an increase in the soil cation exchange capacity and specific surface area in a degraded grassland ecosystem [17]. Lee et al. found that increases in the soil surface potential and electric field intensity could easily induce

the disintegration of soil aggregates [18]. Li et al. conducted sand column tests and found that the barrier effect of Ca^{2+} on colloid is more obvious than that of Na^+ , and that soil colloids can also inhibit ammonia nitrogen migration [19]. Therefore, an accurate and profound understanding of the electrochemical properties of soil colloid surface and the response to the evolution of ecological processes is of great significance for the prevention and control of soil erosion, soil management and regulation, and vegetation restoration and reconstruction [20-22].

However, to date, a little research on soil and water loss characteristics, distribution characteristics and change rules of soil nutrients, and vegetation restoration and reconstruction of karst rocky desertification ecosystem in Southwest China has been conducted [23-25]. However, the electrochemical properties of soil colloids in karst ecosystems, and the response of these properties to the evolution of rocky desertification remains unknown. Soil surface electrochemical properties in karst ecosystems, the response to the process of rocky desertification, and its internal driving mechanism are poorly understood, which seriously limits effective scientific management of karst rocky desertification ecosystems.

This has been investigated the characteristics of electrochemical properties of the soil surface in different grades of rocky desertification, and discussed the response of soil colloid surface electrochemical attribute characteristics to the evolution of rocky desertification and the correlation between physical and chemical influencing factors. This could provide a reference for soil and water flow in a karst rocky desertification ecosystem in Southwest China, and for Soil erosion control, soil management and regulation, and restoration and reconstruction of degraded vegetation.

Materials and Methods

Experimental Site

Huajiang, which is a typical rocky desertification region in the South China karst area, was selected as an experimental site. The location and basic information of the site was presented in Fig. 1. The study area is a typical karst rocky desertification area composed of argillaceous limestone and dolomitic limestone, and the soil is mainly limestone soil. The total study area was 47.91 km², and the altitude ranged from 450-1450 m. The climate type is subtropical mountainous monsoonal

with a mean annual temperature of 18.4°C. Vegetation in the study area included: *Sabina chinensis*, *Pinus massoniana*, *Cyclobalanopsis glauca*, *Zanthoxylum bungeanum*, *Rosa roxbunghii*, *Pyracantha angustifolia*, and *Nephrolepis auriculata*.

Sample Setting and Collection

Based on Jiang et al. [7], the criteria for assigning the degree of degradation were: (1) nil: bedrock exposure rate was <30% and vegetation coverage rate was >70%; (2) slight: bedrock exposure was 30-50% and vegetation coverage was 40-70%; (3) moderate: bedrock exposure was 50-70% and vegetation coverage was 20-40%; (4) severe: bedrock exposure rate was >70% and vegetation coverage was <20%.

Aiming at four typical degrees of rocky desertification, 10 sample plots for each degree of rocky desertification were established, each with an area of 10 × 10 m, with a total of 40 samples. Three sample points were selected using the S-shaped method at the center of each plot, and the distance between the points

was <3 m. Three replicate soil samples were collected at each point from depths of 0-10, 10-15, and 15-20 cm using ring knives and were then mixed into a single sample for testing.

Determination of Soil Surface Electrochemical Properties

Electrochemical properties of soil surface were determined by way of combined surface properties analyses [26-27]. Briefly, the procedures were as follows: First, H⁺ saturated samples were prepared, whereby approximately 100 g soil was washed four times with 500 mL 0.1 mol L⁻¹ HCl, and was then washed repeatedly with deionized water until the suspension was free of Cl⁻. The soil samples were then dried at 60°C and passed through a 0.25-mm sieve. Second, 5 g of H⁺-saturated soil samples (triplicates) were transferred into 150 mL triangular bottles, and 55 mL 0.01 mol L⁻¹ NaOH and Ca (OH)₂ solution was added. After shaking for 24 h, 1 mol L⁻¹ HCl was added to adjust the suspension pH to 7. After shaking for 24

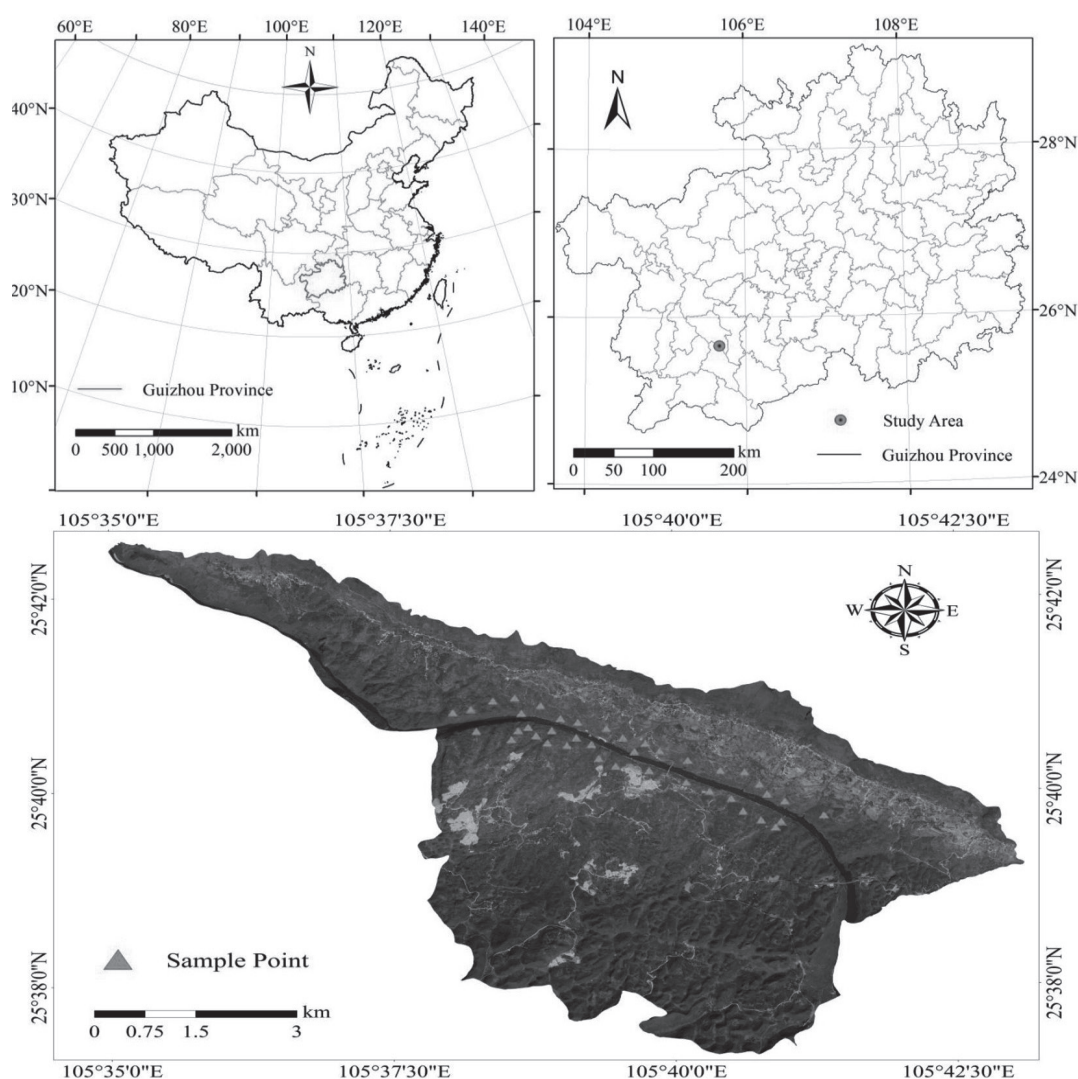


Fig. 1. Location of study area and sample sites, Southwest China.

h, the suspension reached the cation exchange reaction equilibrium, and the final pH was approximately 7. Third, the supernatant was collected after centrifugation and the Ca^{2+} and Na^+ concentrations in the supernatant was determined using atomic absorption spectrometry (Thermo Scientific ICE3000, America). Then, the quantities of Ca^{2+} and Na^+ adsorbed onto soil particles were determined. Finally, the surface electrochemical properties of soil samples were determined using the following equations.

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

$$\sigma_0 = \text{sgn}(\varphi_0) \sqrt{\frac{\varepsilon RT}{2\pi} \left[a_{\text{Na}}^0 \left(e^{\frac{\beta_{\text{Na}} F \varphi_0}{RT}} - 1 \right) + a_{\text{Ca}}^0 \left(e^{\frac{2\beta_{\text{Ca}} F \varphi_0}{RT}} - 1 \right) \right] + (a_{\text{Na}}^0 + 2a_{\text{Ca}}^0) \left(e^{\frac{F \varphi_0}{RT}} - 1 \right)} \quad (2)$$

$$E_0 = \frac{4\pi}{\varepsilon} \sigma_0 \quad (3)$$

$$S = \frac{N_{\text{Na}} K}{m a_{\text{Na}}^0} e^{\frac{\beta_{\text{Na}} F \varphi_0}{2RT}} \times 10^{-2} \quad (4)$$

$$SCN = 10^5 \frac{S \sigma_0}{F} \quad (5)$$

Here, φ_0 (mV) is surface potential; R (J/mol/K) is a gas constant; T (K) is the absolute temperature; F is the Faraday constant (C/mol); a_{Ca}^0 , a_{Na}^0 is the activity of Ca^{2+} and Na^+ in bulk solution, respectively; N_{Na} and N_{Ca} are the numbers of Ca^{2+} and Na^+ adsorbed on the soil particle surfaces, respectively; $\beta_{\text{Ca}} = -0.0213 \ln(I^{0.5}) + 1.2331$, $\beta_{\text{Na}} = 0.0213 \ln(I^{0.5}) + 0.7669$; I is the ionic strength in bulk solution; σ_0 (C/m²) is the surface charge density; ε is the dielectric constant (8.9×10^{-10} C²/J/dm); E_0 (10⁸ V/m) is the surface electric field intensity; S (m²/g) is the specific surface area, $m = 0.5259 \ln(c_{\text{Na}}^0 / c_{\text{Ca}}^0) + 1.992$; c_{Ca}^0 and c_{Na}^0 are the equilibrium concentrations of Ca^{2+} and Na^+ in bulk solution, respectively; K (1/dm) is the Debye parameter, where $K = (4\pi F^2 \sum Z_i^2 a_i^0 / \varepsilon RT)^{1/2}$, and SCN (cmol(-)/kg) is the surface charges number.

Physical, Chemical, and Organic / Inorganic Colloids Properties of Soils

Soil bulk density, natural moisture content, and capillary porosity were measured by the ring knives method. Total porosity was calculated by the formula $P_t = 93.947 - 32.995 \times b$, where b is soil bulk density and P_t is total porosity. All these soil physical properties were described by Ma [28].

Soil particle composition was determined using an hydrometer method (TM-85, Shanghai, China). Soil pH was determined at a 1:2.5 water:soil ratio using a pH electrode (Leici PHS-25, Shanghai, China). The soil organic carbon (SOC) content was determined by the potassium dichromate oxidation-ferrous sulfate titrimetry method, soil total nitrogen (TN) was measured by the Kjeldahl method (Haineng K9840, Jinan, China), and soil total phosphorus (TP) determined by the UV spectrophotometric method (Jingmi UV6100, Shanghai, China). Soil available nitrogen (AN) was measured by the alkaline desorption diffusion method, and soil available phosphorus (AP) was measured by the sodium bicarbonate method. All these soil physical properties were described by Lu [29].

Soil humic acid (HA), fulvic acid (FA), humin (HM), and the ratio of humic acid and fulvic acid (HA/FA) were determined by the potassium dichromate oxidation-ferrous sulfate titrimetry method. Soil free iron oxide (Fe_d) and free alumina (Al_d) were extracted by the sodium bisulfite sodium citrate sodium bicarbonate solution method, amorphous alumina (Al_o) and amorphous silica (Si_o) were tested by the hot alkali solution method, and amorphous iron oxide (Fe_o) was determined by the acidic ammonium oxalate solution method. All these soil organic/inorganic colloids properties were described by Lu [29]. Clay minerals were tested by X-ray diffraction (Smartlab ragiku 2019, Japan) and the detailed steps were similar to those described by Zhao et al. [30].

Data Analysis

Differences in soil electrochemistry, physical, chemical, and organic/inorganic colloids properties between soils under different degrees of rocky desertification were compared using one-way ANOVA and post-hoc test. Correlations between soil electrochemical properties and soil physical, chemical, and organic/inorganic colloids properties were analyzed by the correlation analysis method. Principal component analysis of the rocky desertification ecosystem was also conducted. All statistical analyses were conducted using SPSS22.0 software. Redundancy analysis (RDA) in software canoco5.0 was used to rank the importance of soil factors on surface electrochemical properties.

Result

Characteristics of Electrochemical Properties of Different Rocky Desertification Soils

The soil surface potential, surface charge density, surface electric field intensity, specific surface area, and surface charge number in different grades of rocky desertification soil were shown in Fig. 2 and Table 1. Soil surface potential ranged from -94.28 mV to -107.24

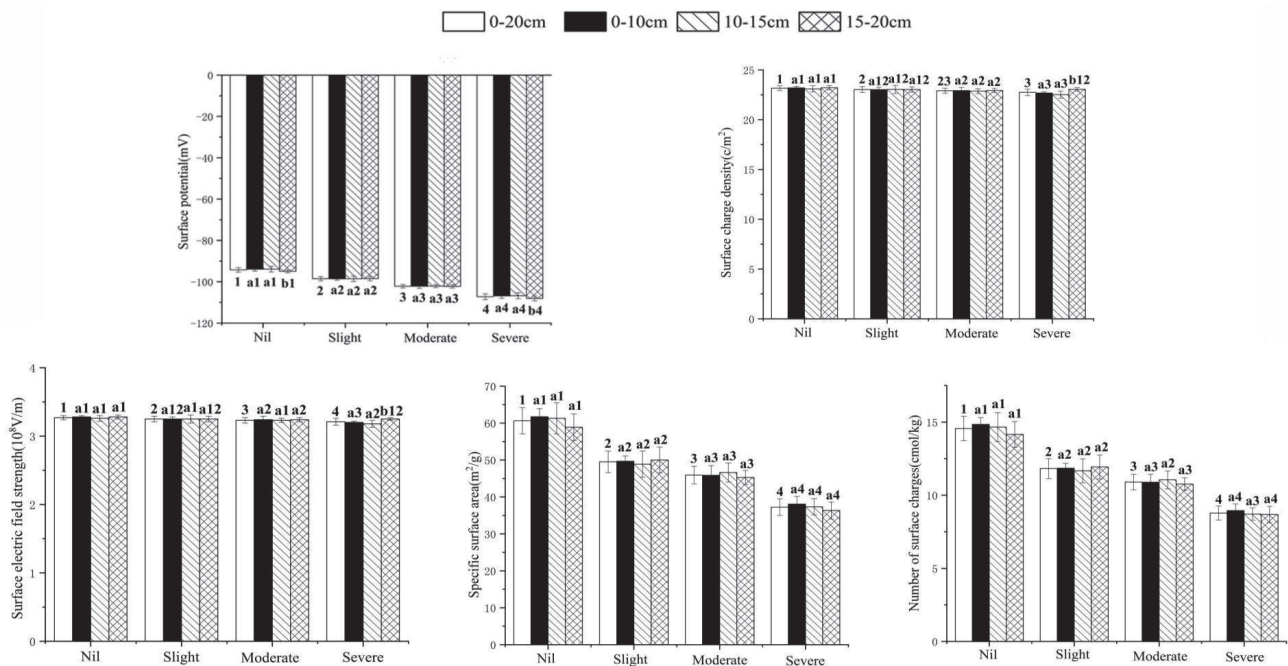


Fig. 2. Soil electrochemical properties under different degrees of rocky desertification.

Lowercase letters indicate the differences of soil surface electrochemical properties in the different soil layer under same rocky desertification grades; the same letter means no significant difference ($p>0.05$), and different letters indicate significant differences ($p<0.05$). Numbers indicate the difference in the surface electrochemical properties in the same soil layer under different rocky desertification grades; the same number means no significant difference ($p>0.05$), and different numbers mean significant difference ($p<0.05$).

mV, and the mean value was -100.56 mV. Under severe rocky desertification, the soil surface potential in the 15-20 cm layer was significantly higher than that in the 0-10 cm and 10-15 cm soil layers ($p<0.05$). The difference of surface potential was not significant between 0-10 cm, 10-15 cm, and 15-20 cm soil layers under other (nil, slight, moderate) rocky desertification grades ($p>0.05$). Soil surface potential increased with the increase of the rocky desertification grade, and the differences between soil in the same profile were significant ($p<0.05$).

Soil surface charge density varied from $22.75 \times 10^{-2} \text{ C/m}^2$ to $23.17 \times 10^{-2} \text{ C/m}^2$, and the mean value was $22.96 \times 10^{-2} \text{ C/m}^2$. Under severe rocky desertification, soil surface charge density in the 15-20 cm layer was significantly higher than that in the 0-10 cm and 10-15 cm soil layers ($p<0.05$). The difference of surface charge density was not significant between 0-10 cm,

10-15 cm, and 15-20 cm soil layers under other (nil, slight, moderate) rocky desertification grades ($p>0.05$). Soil surface charge density decreased with the increase of rocky desertification grades, and in the 0-20 cm, 0-10 cm, and 10-15 cm layers it was significantly higher than in the same soil profile under other (slight, moderate) rocky desertification grades ($p<0.05$).

Soil surface electric field strength ranged from $3.21 \times 10^8 \text{ V/m}$ to $3.27 \times 10^8 \text{ V/m}$, and the mean value was $3.24 \times 10^8 \text{ V/m}$. Under severe rocky desertification, the soil surface electric field strength in the 15-20 cm layer was significantly higher than that in the 0-10 cm and 10-15 cm soil layers ($p<0.05$). Soil surface electric field strength decreased with the increase of rocky desertification grades, and decreased significantly ($p<0.05$) in the 0-20 cm soil layer under different rocky desertification grades (nil, slight, moderate, severe). Soil surface electric field strengths in the 0-10 cm and

Table 1. Electrochemical properties of different soil layers.

Index	Φ_0 (mV)	σ_0 (10^{-2} C/m^2)	E_0 ($10^8 \text{ V} \cdot \text{m}^{-1}$)	S (m^2/g)	SCN ($\text{cmol}(-)/\text{kg}$)
0-10 cm	-100.40±4.89a	22.95±0.29a	3.24±0.04ab	48.83±8.89a	11.63±2.20a
10-15 cm	-100.33±4.93a	22.88±0.39a	3.23±0.05b	48.53±9.20a	11.52±2.56a
15-20 cm	-100.95±5.00a	23.05±0.23a	3.26±0.03a	47.62±8.71a	11.38±2.12a

The same letter indicates that indicator has no significant difference under different rocky desertification grades ($p>0.05$), while different letters indicate that indicator has significant difference under different rocky desertification grades ($p<0.05$).

Table 2. Physical properties of soil among different rocky desertification grades.

Degree of rocky desertification	Bulk density	Total porosity (%)	Capillary porosity (%)	Natural moisture content (%)	Sand (%)	Silt (%)	Clay (%)
Nil	1.12±0.05c	56.85±1.7a	36.11±1.29a	25.72±1.18a	19.50±1.29d	56.39±0.96a	24.11±0.91a
Slight	1.14±0.06c	56.40±1.98a	35.33±1.24b	24.75±0.99b	23.26±1.03c	55.09±0.93b	21.65±0.93b
Moderate	1.17±0.03b	55.34±1.13b	34.52±1.18c	24.19±1.12c	28.22±1.15b	52.28±0.75c	19.50±0.90c
Severe	1.25±0.05a	52.78±1.75c	32.41±1.45d	22.20±1.18 d	31.33±1.43a	52.68±1.17c	15.99±0.71d

The same letter indicates that indicator has no significant difference under different rocky desertification grades ($p > 0.05$), while different letters indicate that indicator has significant difference under different rocky desertification grades ($p < 0.05$).

15-20 cm soil layers under the nil rocky desertification grade were significantly higher than those in the same soil profile under the moderate rocky desertification grade ($p < 0.05$). Soil surface electric field strength in the 0-10 cm and 10-15 cm soil layers under nil rocky desertification grade were significantly higher than that in the same soil profile under the severe rocky desertification grade ($p < 0.05$).

The specific surface area varied from 37.24 m²/g to 60.63 m²/g, and the mean value was 48.33 m²/g. The specific surface area significantly decreased ($p < 0.05$) with an increase in the rocky desertification grade.

Soil surface charges numbers ranged from 8.78 cmol(-)/kg to 14.56 cmol(-)/kg, and the mean value was 11.51 cmol(-)/kg. The differences of the soil surface charges number within the different soil layers under same rocky desertification grade were not significant ($p > 0.05$).

Characteristics of Physical, Chemical, and Organic/Inorganic Colloid Properties under Different Rocky Desertification Grades

In Table 2, comparisons of soil physical properties between different grades of rocky desertification show significant differences in soil bulk density between different degrees of rocky desertification. Specially, the soil bulk density of severe rocky desertification was significantly greater than that of soils in areas with other degree of desertification. This study show significant differences in soil porosity between different degrees

of rocky desertification. Specifically, soil total porosity in areas with moderate and severe rocky desertification was significantly less than in soils with other grades of desertification. There were significant differences in soil capillary porosity observed among the four grades of rocky desertification, and soil capillary porosity in soil with severe rocky desertification was significantly less than that of other rocky desertification grades; the same law can be found in the soil natural moisture content in this study (Table 2). The results also reveal significant difference in soil particle size composition between different grades of rocky desertification, whereby the soil sand content increased with increases in the rocky desertification grade, and the opposite was found in the soil silt and clay contents between different rocky desertification grades.

As shown in Table 3, soil C, N, P, AN, and AP decreased with the increase of rocky desertification grade, and there were significant differences in these indicators among different rocky desertification grades ($p < 0.05$). However there were no significant differences in soil pH among different rocky desertification grades ($p > 0.05$).

Table 4 shows decreasing trends in soil HA, FA, HM, HA/FA, Al_o, and iron activity with an increase of the rocky desertification grade, and there were significant differences in these indicators among different rocky desertification grades ($p < 0.05$). Fe_d increased with the increase in the rocky desertification grade, and significant differences existed between different grades ($p < 0.05$). The soil Al_d content of

Table 3. Chemical properties of soil among different rocky desertification grades.

Degree of rocky desertification	Organic carbon (g/kg)	Total nitrogen (g/kg)	Total phosphorus (g/kg)	Available nitrogen (mg/kg)	Available phosphorus (mg/kg)	pH
None Nil	32.28±1.35a	4.51±0.43a	0.71±0.03a	230.27±10.68a	5.06±0.35a	7.40±0.11a
Slight	28.08±1.15b	3.61±0.46b	0.64±0.02b	179.20±9.67b	5.15±0.26a	7.41±0.19a
Moderate	25.58±1.42c	3.30±0.42c	0.59±0.02c	149.71±5.22c	3.88±0.37b	7.46±0.09a
Severe	19.63±1.04d	3.14±0.29c	0.42±0.03d	96.68±8.64 d	3.10±0.18c	7.44±0.22a

The same letter indicates that indicator has no significant difference under different rocky desertification grades ($p > 0.05$), while different letters indicate that indicator has significant difference under different rocky desertification grades ($p < 0.05$).

Table 4. Organic/inorganic colloid properties of soil among different rocky desertification grades.

Degree of rocky desertification	Humic acid (g/kg)	Fulvic acid (g/kg)	Humic acid (g/kg)	HA/FA	Fe _d (g/kg)	Al _d (g/kg)	Fe _o (g/kg)	Al _o (g/kg)	Fe _d /Fe _o (%)
Nil	6.22±0.21a	9.38±0.31a	16.68±1.39a	0.66±0.03a	15.48±0.67d	9.35±0.67a	1.57±0.25b	1.99±0.26a	10.16±1.62a
Slight	4.74±0.23b	7.87±0.29b	15.47±1.13b	0.60±0.04b	18.32±0.83b	7.54±0.67c	1.79±0.29a	1.67±0.19b	9.80±1.62a
Moderate	3.59±0.17c	7.04±0.18c	14.95±1.39c	0.51±0.03c	19.67±0.54bc	7.33±0.75c	1.50±0.28b	1.47±0.19c	7.63±1.46b
Severe	1.49±0.07d	5.21±0.25d	12.93±0.98d	0.29±0.02d	20.34±0.95a	8.03±0.58b	1.32±0.22c	1.38±0.26c	6.50±1.19c

The same letter indicates that indicator has no significant difference under different rocky desertification grades ($p > 0.05$), while different letters indicate that indicator has significant difference under different rocky desertification grades ($p < 0.05$).

severe rocky desertification (mean of 8.03 g kg⁻¹) was significantly higher than that of slight and moderate rocky desertification grades (means of 7.54 g kg⁻¹ and 7.33 g kg⁻¹, respectively). The soil Fe_o content in 0-20 cm layer soil under different rock desertification showed a slight>nil>moderate>severe. There were significant differences in soil Fe_o among different grades ($p < 0.05$). Soil Si_o content in 0-20 cm layer soil under different rock desertification showed nil>severe>slight>moderate, and significant differences were observed among different rocky desertification grades ($p < 0.05$).

Under the four rocky desertification grades, we randomly selected three groups of soil profiles under each rocky desertification grade, with a total of 36 soil samples identified for clay mineral composition, and the mean values are shown in Table 5. The soil illite content decreased with the increase in the rocky desertification grade, while the kaolinite and green montmorillonite contents in the mixed layer decreased with the increased rocky desertification grade.

Correlation between Soil Surface Electrochemical Properties and Soil Physicochemical Properties and Organic/Inorganic Colloids

The soil surface potential, surface charge density, surface electric field strength, specific surface area, and surface charge number were all positively correlated with total porosity, capillary porosity, natural water content, silt and clay particles ($p < 0.01$), and were negatively correlated with soil bulk density and sand particles ($p < 0.01$) (Table 6).

Table 7 shows that the soil surface potential, specific surface area, and surface charge number were positively correlated with SOC, TN, TP, AN, and AP ($p < 0.01$). Soil surface charge density and surface electric field strength were positively correlated with SOC, TN, TP, AN, and AP ($p < 0.01$).

Soil surface potential, specific surface, and surface charge number were positively correlated with HA, FA, HM, HA/FA, Al_d, Fe_o, Al_o, and iron activity ($p < 0.01$), and negatively correlated with Fe_d ($p < 0.01$). Soil surface charge density was positively correlated with HA, FA, HM, HA/FA, Al_d, Al_o, and iron activity ($p < 0.01$), and negatively correlated with Fe_d ($p < 0.01$). Soil surface electric field intensity was significantly positively correlated with HA, FA, HA/FA, Al_o, and iron activity ($p < 0.01$), positively correlated with Al_d ($p < 0.05$), and negatively correlated with Fe_d ($p < 0.01$).

Principal Component Analysis of Rocky Desertification Based on Soil Surface Electrochemical Characteristics and Its Influencing Factors

From the correlation analysis in Table 6, a total of 20 soil physical and chemical indexes and organic/inorganic colloid indexes were significantly correlated

Table 5. Soil clay mineral composition among different rocky desertification grades.

Grade of rocky desertification	Semectite (%)	Illite / (%)	Kaolinite / (%)	Chlorite / (%)	Illite/Semectite/ (%)	Chlorite/Semectite/ (%)
Nil	0	6.46	5.93	3.10	2.78	82.44
Slight	0	4.14	6.16	3.76	5.72	83.06
Moderate	0	2.29	6.70	2.53	1.00	87.48
Severe	0	3.50	6.97	3.66	1.04	87.56

with 5 soil electrochemical properties. Therefore, the principal component analysis of rocky desertification was carried out based on 25 indicators of soil surface electrochemical properties and their influencing factors. The contribution rate of principal component 1 was 69.49%, that of principal component 2 was 7.10%, and the cumulative contribution rate was 76.58%. With the first principal component value as the abscissa and the second principal component value as the ordinate, scatter plots of 25 indicators and 4 typical grades of rocky desertification were constructed (Fig. 3).

The results show that the soil surface charge density, surface electric field strength, and surface charge number were significantly correlated with HA, FA, Al_d , Al_o , silt, clay, TN, and AN, which were important factors for characterizing nil rocky desertification. Soil bulk density was closely related to slight rocky desertification. Sand and Fe_d were closely related to moderate rocky desertification. Soil surface potential

and specific surface area were significantly correlated with HM, HA/FA, iron activity, total porosity, capillary porosity, natural water content, organic carbon, TP, and AP, which were important factors to characterize severe rocky desertification.

Importance Ranking of Factors on Soil Surface Electrochemical Properties

In order to distinguish the influence of 20 kinds of soil physical and chemical factors on soil surface electrochemical properties, Redundancy analysis has been performed by using Canoco5.0 software. A total of 91.69% of the soil surface electrochemical properties were explained by 20 factors in the first two sorting axes of the RDA. As shown in Table 7, the effect of the selected 20 indexes on soil surface charge properties reached a significant level ($p = 0.02$), indicating that the selected influencing factors can better reflect the differences in soil surface charge properties.

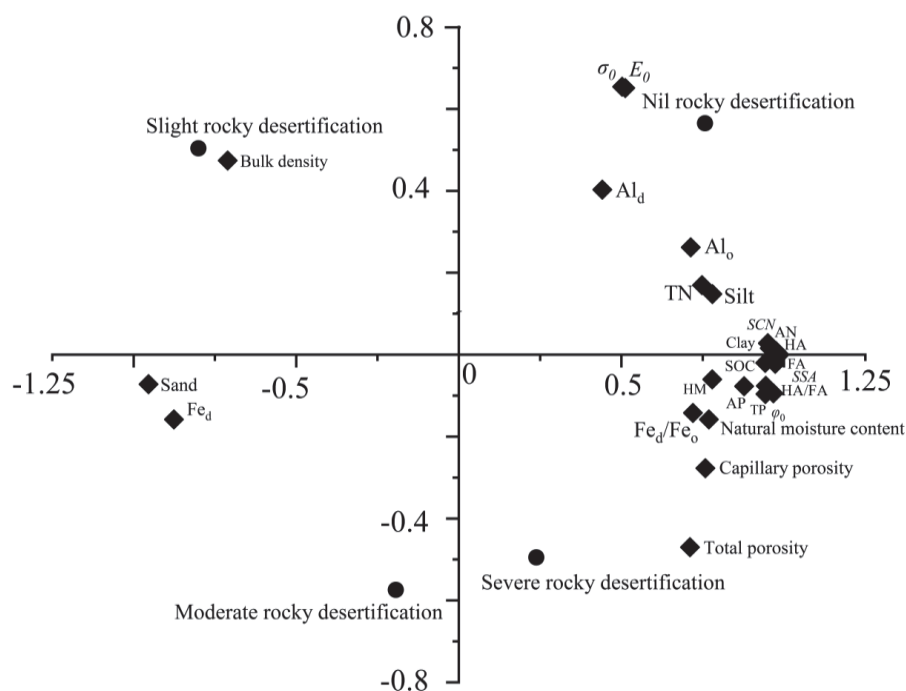


Fig. 3. Scatter diagram of principal component analysis for karst rocky desertification (x axis, value of component 1; y axis, value of component 2).

Table 6. Correlation between soil surface electrochemical properties and soil physicochemical properties and soil organic/inorganic colloids.

Index	Soil physical attributes factor						Soil chemical attributes factor						
	Bulk den- sity	Total po- rosity	Capillary porosity	Natural moisture content	Sand	Silt	Clay	SOC	TN	TP	AN	AP	pH
Electrochemical indicators													
φ_0	-0.660**	0.661**	0.708**	0.743**	-0.938**	0.762**	0.943**	0.939**	0.699**	0.924**	0.964**	0.863**	-0.104
σ_0	-0.224**	0.244**	0.324**	0.312**	-0.456**	0.355**	0.469**	0.475**	0.399**	0.448**	0.447**	0.425**	-0.030
E_0	-0.246**	0.246**	0.329**	0.320**	-0.464**	0.355**	0.481**	0.485**	0.405**	0.456**	0.456**	0.435**	-0.023
S	-0.626**	0.626**	0.666**	0.712**	-0.896**	0.735**	0.897**	0.913**	0.722**	0.871**	0.973**	0.767**	-0.068
SCN	-0.624**	0.624**	0.668**	0.713**	-0.902**	0.739**	0.903**	0.919**	0.732**	0.876**	0.942**	0.774**	-0.068
Soil organic/inorganic colloidal factors													
Index													
Electrochemical indicators	Humic acid	Fulvic acid	Humin	HA/FA	Fe _d	Al _d	Fe _o	Al _o	Fe _d /Fe _o				
φ_0	0.970**	0.995**	0.720**	0.930**	-0.860**	0.424**	0.389**	0.637**	0.693**				
σ_0	0.485**	0.473**	0.378**	0.467**	-0.413**	0.236**	0.090	0.437**	0.257**				
E_0	0.497**	0.484**	0.385**	0.479**	-0.427**	0.230*	0.098	0.445**	0.269**				
S	0.993**	0.924**	0.714**	0.875**	-0.860**	0.473**	0.319**	0.654**	0.640**				
SCN	0.940**	0.931**	0.719**	0.881**	-0.866**	0.479**	0.314**	0.668**	0.638**				

Sample size N=120

*** indicates significant $\alpha=0.05$ and 0.01 levels, respectively.

Table 7. Importance ranking and significance test results of soil physical and chemical factor interpretation.

Rank	Indicators	Interpretation rate (%)	Importance	Rank	Indicators	Interpretation rate (%)	Importance
1	AN	89	956	11	Natural moisture content	51.7	126
2	HA	88.6	921	12	TN	51.5	125
3	FA	86.7	771	13	Silt	51.5	125
4	SOC	84.5	642	14	HM	51.3	124
5	Clay	82.4	551	15	Capillary porosity	45.7	99.2
6	HA/FA	79.0	445	16	Fe _d /Fe _o	43.1	89.2
7	TP	78.3	426	17	Al _o	42.4	86.9
8	Fe _d	74.0	337	18	Bulk density	40.2	79.3
9	AP	62.4	196	19	Total porosity	40.2	79.3
10	Silt	54.9	144	20	Al _d	21.4	32.2

Discussion

Electrochemical Properties of Karst Soil Surface and the Response to Rocky Desertification Evolution

During the process of increasing the rocky desertification level, the above ground and underground soil loss caused by hydraulic and gravity intensifies, the rock exposure rate increases, and the soil barren and aboveground biomass decrease, forming a destructive cycle [1], which leads to significant decreases in SOC, HA, and FA. At the same time, soil HA/FA decrease with the increase in the rocky desertification grade. At the same time, losses of soil clay and silt in karst rocky desertification areas increase with soil erosion [31]. In this study, with increases in the rocky desertification grade, soil becomes coarse, bulk density increased, and total porosity, capillary porosity, and natural water content decreased (Table 2). Fe_d is often used to reflect the soil forming process and its environment, and is an indicator of the degree of soil weathering [32]. Due to the high degree of weathering, the Fe_d content in the severe rocky desertification area was higher than that in the non-rocky desertification area. At the same time, the aging degree of iron oxide was higher, and iron activity was relatively low (Table 4). Illite in soil clay minerals is easily preserved and accumulated in the environment due to weak weathering and leaching, while kaolinite indicates a strong leaching, weathering, and soil-forming environment [33]. The illite content in soil clay minerals in the severe rocky desertification area was relatively low, and the kaolinite content was higher, which also indicates that the intensities of weathering and leaching are higher in this area.

The environmental characteristics are the main reasons for the decreases in the surface charge density, surface electric field intensity, specific surface area and surface charge quantity with an increase in

the rocky desertification grade. In this study, the differences between surface electric field intensity, specific surface area, and surface charge of nil rocky desertification soil were 0.06×10^8 V/m, 23.38 m²/g, and 5.78 cmol(-)/kg, respectively. According to Rakhsh et al. [34], soil surface electrochemical properties have important indicative significance in characterizing the ion exchange and diffusion processes of the soil solid-liquid interface. Therefore, the differences in the soil electrochemical properties in this study can explain that the soil adsorption and desorption capacity of ions and components, and the retention and interaction ability of nutrient elements, declined due to the aggravation of rocky desertification.

Effects of Soil Physical and Chemical Properties on Soil Surface Electrochemical Properties of Karst Rocky Desertification

Tables 2 and 3 show that soil electrochemical properties are mainly affected by SOC and particle size composition. In this study, SOC was positively correlated with surface electrochemical properties, which was consistent with previous results [17, 27]. At present, the relationship between organic matter and organic carbon is converted by the van Bemmelen factor [35]. Therefore, soil organic matter is also positively correlated with surface electrochemical properties. The honeycomb structure of organic matter and the rich active groups such as carboxyl, hydroxyl, and aldehyde groups on the surface of organic matter result in the soil organic matter having a huge specific surface area and charge, and provides a large number of cation replacement points [17]. Clay has a huge specific surface area, and its main component is layered silicate clay minerals and oxides, which can cause a negative charge on the soil surface through isomorphic replacement and hydroxyl ion dissociation [36], and, therefore, it is positively correlated with electrochemical properties.

Sand particles are mostly primary minerals with a small specific surface area and have less ion exchange sites than clay [37], therefore, it was negatively correlated with electrochemical properties. At the same time, soil water content has an important impact on plant growth in the karst rocky desertification area. Soil with a low water content is not conducive to plant growth, and compared with the severe rocky desertification area, the well-formed soil structure in the nil rocky desertification area increases the soil water holding capacity, and plants with good growth ensure the accumulation of soil organic matter mainly from their litter [38-39]. This is one of the important reasons for the high electrochemical properties of soil in the study area.

In addition, pH changes can also affect the electrochemical properties of the soil surface [40]. However, there were no significant differences in soil pH under different rocky desertification intensities in the study area (Table 2). Therefore, pH is not an important factor affecting the electrochemical properties of the soil surface in this study, which is consistent with the results of Liu et al. [17].

Effects of Soil Organic/Inorganic Colloidal Properties on Soil Surface Electrochemical Properties of Karst Rocky Desertification

Tables 4 and 7 show that the soil electrochemical properties are mainly affected by the composition of humus and metal oxides. Soil humus has a huge specific surface area of 800-900 m²/g, which is more than 10 times larger than that of inorganic minerals in soil [37]. HA, FA, and HM have organic surfaces, and surface functional groups such as hydroxyl, carboxyl, and quinone groups can create a negative charge on the soil surface by dissociating H⁺ [41]. It was found that with the increase in the rocky desertification grade, soil HA, FA, and surface electrochemical properties (except surface potential) showed the same trend, and, therefore, humus was an important contributor to soil surface electrochemical properties.

Fe_a, Fe_o, and Al_o are the major oxides and related indicators that have significant impacts on soil surface electrochemistry [42]. Soil Fe_a is an important carrier of a variable charge in soil [43]. With an increase in the rocky desertification grade, the soil Fe_a content increased, whereas the soil clay, SOC, HA, FA, and other indicators which explained the electrochemical changes of soil surface, decreased (Table 3). The contribution rate of Fe_a to the change of soil surface electrochemical properties was lower than that of organic matter and humus (Table 7). This view is consistent with Salazar et al. [44], but contrary to Ketrot et al. [45], which may be due to differences in the adsorption and complexation strength of clay minerals and metal oxides on organic matter in different soils [46-47]. Therefore, there were negative correlations between the Fe_a and related electrochemical properties (Table

6). In addition, Fe_o and Al_o have large specific surface areas, strong reaction activity, and high cation specific adsorption capacity [48]. In this study, soil amorphous metal oxides and soil surface electrochemistry showed the same change trend, and, therefore, were positively correlated.

Implications of Physical and Chemical Soil Surface Electrochemical Characteristics on Restoration and Reconstruction of Rocky Desertification Degraded Ecosystems

For a long time, researchers have focused on the physical and chemical factors, soil physical indicators, and nutrient chemical indicators in the process of karst rocky desertification succession, and have addressed the surface causes of soil fertility decline, such as soil erosion aggravation, bedrock exposure, and the weakening of bioaccumulation [49-50]. However, the important roles of soil colloids in nutrient absorption, migration, and transformation have been ignored. In this study, soil free metal oxides were enriched in the soil during the increase in the rocky desertification grade (Table 4). However, the contents of soil organic matter, humus and clay decreased with the increase of rocky desertification grade, and in this study, their contribution to the electrochemical properties of soil surface was higher than that of free metal oxides (Table 7), which eventually led to declines in soil fertility retention, storage, and supply capacity.

This study shows that the decrease of SOC is an important cause of the decline in soil surface charge properties with the intensification of rocky desertification. In recent years, biochar and nano carbon have achieved fruitful results in regulating soil physicochemical properties [51-52]. Carbon auxiliary materials can effectively reduce soil bulk density and increase the SOC content [53]. Such additions will also increase the surface area of organic colloids in soil and enhance the soil charge properties, which provides a novel means of improving the ability of soil to maintain and supply fertilizer and accelerate the recovery of rocky desertification ecosystems.

In addition, it was found that the change in the electrolyte concentration in soil bulk solution would disturb the electrical double layer structure of soil particles and subsequently affect the physical erosion process of soil. Yu et al. found that when the soil surface potential is <153 mV [54], disturbance of the soil electric field on the stability of soil aggregates is the main mechanism affecting soil water movement. Hu et al. found that an increase in the soil electric field will cause strong hydration and electrostatic repulsion between particles after the electrolyte is diluted with water [55], and that the greater the dilution degree is, the greater the aggregate rupture strength will be, which will induce soil erosion. In this study, the electric field intensity of soil surface increased with the increase in the rocky desertification grade (Fig. 2), which means

that soil aggregates in severe rocky desertification areas are exposed to stronger electric field disturbance. At the same time, the soil water content in the severe rocky desertification area was lower than those in other rocky desertification areas (Table 2). When precipitation occurs, if regional soil moisture content rises to the same value, the electrolyte dilution degree of the soil in the severe rocky desertification area is higher than that in other areas, and the soil particles will inevitably produce stronger hydration and electrostatic repulsion forces, which makes it easier for soil to agglomerate and disintegrate, thus increasing the risk of water and soil loss. Therefore, soil erosion prevention and control in karst rocky desertification areas from the perspective of soil surface electrochemical characteristics should be the focus of future research.

Conclusions

Rocky desertification has important impacts on soil physical and chemical properties, soil organic/inorganic colloid content, and soil surface electrochemical properties. With the increase in the rocky desertification grade, the soil physical structure deteriorated, the contents of SOC, TN, TP, HA, and FA decreased, and the content of free metal oxides increased. Increases in the rocky desertification level have a negative impact on the electrochemical properties of soil surface. The results showed that the surface charge density, surface electric field strength, specific surface area, and surface charge quantity were significantly positively correlated with the contents of humus, clay, and sand, and negatively correlated with Fe_d . The results provide important information regarding the changes in soil electrochemical properties during the process of karst rocky desertification succession, and provide a new perspective for soil quality management and regulation in the process of rocky desertification control.

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Conflicts of Interest

The authors declare no conflicts of interest.

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