

Original Research

Study on the Desorption Behavior and Bioavailability of Polycyclic Aromatic Hydrocarbons in Different Rocky Desertification Soils

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Abstract

Karst desertification areas are extremely fragile ecological environments. The migration and transformation of Polycyclic aromatic hydrocarbons (PAHs) in desertification soils are still rarely studied, and the relevant impact mechanisms remain unclear. The study selected lime soil with different rocky desertification grades in southwestern karst area and phenanthrene and pyrene in the environment as the research objects, and investigated the desorption behavior of PAHs in different rocky desertification soils and the impact mechanism of earthworm bioavailability. The results showed that in severe rocky desertification soil (SRDS), moderate rocky desertification soil (MRDS) and light rocky desertification soil (LRDS), fraction of rapid desorption (F_{rap}) of phenanthrene increased by 18.51%, 14.03% and 9.65%, respectively compared with non-rocky desertification soil (NRDS); F_{rap} of pyrene increases by 15.79%, 5.53% and 4.32%, respectively. The bioavailability fraction (F_{bio}) of PAHs in karst desertification areas was about twice that of Tenax1-6h extraction concentration. The desorption intensity and bioavailability components of PAHs in soils increase with the increase of rocky desertification. Pearson and redundancy analysis (RDA) showed base saturation, porosity and SOC were the main physical and chemical properties that affect the desorption capacity and bioavailability accumulation factors of PAHs in karst soils. Calcium ions in the soil of karst desertification areas may promote the desorption of PAHs.

Keywords: desertification, soil, PAHs, desorption, bioavailability

Introduction

Persistent organic pollution has been widely concerned all over the world. The “Stockholm Convention” stipulates 12 types of persistent organic pollutants (POPs) for priority control, and later the number of POPs on the list increased to 21 [1]. PAHs are typical representatives of persistent organic pollutants. Research reports indicate that China’s PAHs emissions accounted for 22% of global emissions in 2004 [2], and China had about 30,000 tons of PAHs emissions in 2016, with most organic pollutants entering the soil/sediment ecosystem [3]. PAHs are mainly derived from chemical production, motor vehicle emissions, incomplete combustion of fossil fuels and biomass, and other human activities [3-5]. Most PAHs are difficult to degrade naturally, which have high environmental persistence, exist for a long time in the environment and continuously migrate. With low water solubility, high lipophilicity, high bioaccumulation, it can accumulate in organisms and gradually enrich along the food chain [6-10]. The environmental, ecological and health effects of PAHs have received extensive attention from the international community. Studies have reported that the pollution of PAHs in Guiyang, Guizhou is at a moderate level [11]. Yang et al. [12] pointed out that the concentration of PAHs in Guizhou ranges from 2.18 $\mu\text{g/g}$ to 14.20 $\mu\text{g/g}$, with an average of 6.78 $\mu\text{g/g}$. Guizhou is the region with the most extensive and richest distribution of karst landforms in southwest China. Due to the fragile ecological environment, biomass is greatly used in mountainous areas. Coupled with rapid urbanization, rapid growth of motor vehicles, and coal-led energy structure, PAHs accumulation in the soil deteriorates.

There are many factors affecting the adsorption and desorption of PAHs in the soil-water system, including three categories: the physical and chemical properties of the pollutants themselves, environmental factors, and soil characteristics. The molecular structure and size of PAHs and their hydrophobicity are important factors affecting their adsorption and desorption. Lamichhane et al. [13] pointed out that as the molecular weight of PAHs increases, it is more difficult for PAHs to enter the soil microstructure. At the same time, with the increase of PAHs octanol-water partition coefficient, the adsorption capacity of PAHs in the soil increases, and the hysteresis of desorption increases. The environmental factors of the soil have an important impact on the migration and transformation of PAHs. Studies have shown that soil pH will significantly affect the adsorption and desorption behavior of PAHs by changing the surface charge of the adsorbent [14]. Olu-Owolabi et al. [15] believed that higher soil temperature will promote the environmental behavior of PAHs, and may weaken the distribution coefficient K_d of PAHs on the soil substrate. Dissolved organic matter (DOM) in the environment will enhance the desorption capacity of PAHs. Maxin et al. [16] pointed out that adsorption

of DOM hydrophobic component to the soil matrix after combination with PAHs will result in lower migration ability of PAHs. As the contact time between PAHs and the soil matrix increases, PAHs will show a significant aging effect, and pollutant molecules will enter deeper into the soil matrix or enter the microscopic pores of the soil, resulting in lower desorption capacity [17]. Soil property is also an important factor affecting the adsorption and desorption of PAHs. Studies have pointed out that the content and composition of soil organic matter are the main factors affecting the adsorption and desorption of PAHs [18]. Cheng et al. [19] found that the types and contents of soil minerals also significantly affect the adsorption and desorption of PAHs. There are many research reports on the influence of different soils on the adsorption and desorption of PAHs, but the main considerations are soil organic matter [20], mineral types and content [21], and soil aggregates [22, 23]. There is no report on the effect of soil water-soluble ions on desorption, especially in the ecologically fragile karst rocky desertification area where the soil has obvious calcium-enriched characteristics, and the water-soluble calcium content is significantly higher than other soils, so desorption and bioavailability of PAHs may be affected. The purpose of this research is to investigate the influence of calcium-richness of different typical karst rocky desertification lime soils on PAHs desorption and bioavailability, qualitatively and quantitatively analyze the changes of PAHs desorption and bioavailability in different rocky desertification soils, and try to reveal its influence mechanism. The study can fill the research gap in environmental migration behavior of PAHs in karst ecologically fragile areas, and provide references for its ecological risk assessment and related governance.

Materials and Methods

Soil Samples and Pollutants

The study selects lime soils of different karst rocky desertification grades in Guizhou province as the research object. There are two main indicators for different rocky desertification soils: vegetation coverage and rock exposure rate. The specific sampling points are shown in Fig. 1. Four sample quadrats (10 m \times 10 m for each sample quadrat) were selected for soil of each rocky desertification grade. The surface soil of 0-20 cm was collected by snake sampling method. After mixture, the samples were dried naturally in the laboratory, removed with residual roots and gravel, screened through 100-mesh sieve. At the same time, to avoid the mineralization of PAHs by microorganisms in the soil, the air-dried soil was sterilized at 0.1 MPa, 121°C for 30 min, repeated after 24 h, and then sealed at room temperature and stored in a dark place for later use. The pH of the soil was measured by a pH meter (Sartorius professional meter pp-50, Germany)

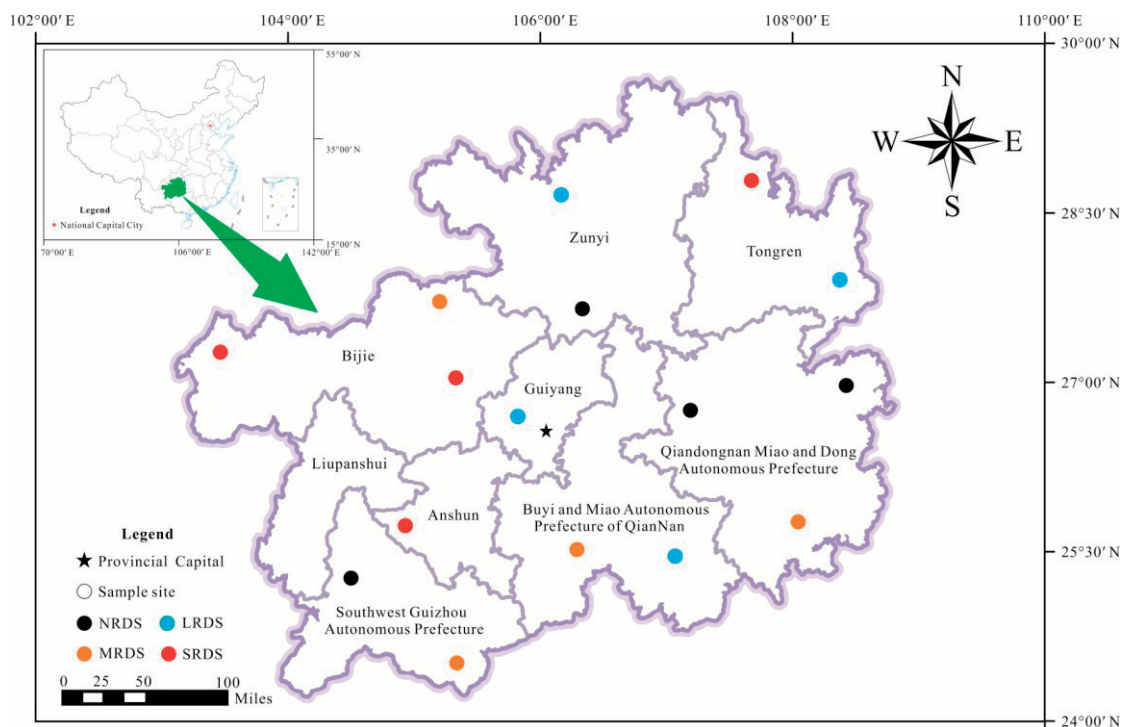


Fig. 1. Distribution of soil sampling sites of different rocky desertification types.

using the mili-Q water solution method (water-soil ratio 1:1) for CO₂ removal. Soil organic carbon was measured using sulfuric acid-potassium dichromate external heating-volumetric titration. The soil base saturation was calculated as the percentage of the total exchangeable base to the cation exchange capacity (the total exchangeable base was measured by neutralization titration, and the cation exchange capacity was measured by the ammonium acetate exchange method). The soil bulk density was measured by the cutting ring method, the moisture content was calculated by the drying method, and the porosity was calculated by the soil bulk density and specific gravity. The soil water-soluble calcium was determined using the EDTA complexometric titration method in the Chinese national standard NY/T3242-2018. The soil specific surface area (SSA) was measured using N₂-BET (Autosorb-iQ,

Quanta chrome, USA). The basic physical and chemical properties of soil are shown in Table 1.

The study selected phenanthrene and pyrene common in nature as the target PAHs. The main physical and chemical properties of the two compounds are as follows. Phenanthrene C₁₄H₁₀, molecular weight 178.08, water solubility 1.15 mg/L, octanol-water partition coefficient Log K_{ow} 4.46; pyrene C₁₆H₁₀, molecular weight 202.25, water solubility 0.137 mg/L, octanol-water partition coefficient Log K_{ow} 5.18 [8].

Adsorption and Desorption Experiments

Previous studies have pointed out that the concentration of phenanthrene and pyrene in industrially polluted soil is basically 150-230 mg kg⁻¹, and the total PAHs concentration can reach 1000 mg kg⁻¹ [24].

Table 1. Basic physical and chemical properties of soil samples.

Soil	pH	SOC (g/kg)	SBD (g/cm ³)	WC (wt%)	DP (%)	BS (%)	WSC (g/kg)	VC (%)	SSA (m ² /g)
NRDS	6.89a	32.6a	2.28a	36.2a	53.3a	25.21a	1.02a	76.8a	23.51a
LRDS	7.02b	25.3b	1.41b	16.38b	46.2b	30.38b	2.15b	46.2b	33.36b
MRDS	7.15c	20.8c	0.38c	28.1b	38.5c	33.63c	3.82c	26.1c	10.17c
SRDS	7.08c	15.3d	1.25d	10.9c	20.6d	32.47d	5.06d	12.7d	16.84d

Note: The data in the same column is marked with different lowercase letters to indicate significant differences between the plots (P<0.05).; NRDS, non-rocky desertification soil; LRDS, light rocky desertification soil; MDRS, moderate rocky desertification soil; SRDS, severe rocky desertification soil. SOC, soil organic carbon; SBD, soil bulk density; WC, water capacity; DP, degree of porosity; BS, base saturation; WSC, water soluble calcium; VC, Vegetation coverage; SSA, Specific surface area.

The total concentration of PAHs in surface soils in China can reach up to 6100 mg/kg, with an average of 30.53 mg/kg [25]. Zhou et al. [26] studied the desorption of PAHs on charcoal and set the concentrations of phenanthrene and pyrene at 1500 mg/kg and 200 mg/kg PAHs as the initial pollution concentration. Zhao et al. [27] studied the aging behavior of PAHs in soil, the concentration of pollutants with standard phenanthrene and pyrene reached 100 mg/kg. In this study, the initial pollution concentration of different rocky desert soils added with phenanthrene and pyrene was 50 mg/kg, which was also close to the actual pollution concentration in the study area.

In the adsorption experiment, due to the quite low solubility of phenanthrene and pyrene in the aqueous solution, 100 mg phenanthrene and 100 mg pyrene were dissolved in 1L hexane to prepare organic stock solutions of phenanthrene and pyrene. Then, 2000 g lime soil was added to the stock solution to make mud. Place the sample on a heating plate ($50\pm 1^\circ\text{C}$) with an interval of 10 min and slowly stir the slurry to ensure that phenanthrene and pyrene can fully contact the soil particles and the pollutants are evenly distributed in the soil, thus boosting the volatilization of hexane. The dried soil containing the target contaminants was then sealed and stored in the dark for later use.

The study used Tenax ball for desorption experiment. Before using Tenax, it was washed by Soxhlet extraction, and washed with acetone, acetone plus hexane, methanol, and acetone for 48 hours in sequence to ensure that the purity of Tenax was close to 0 (the concentration is below the minimum limit of the detection instrument). The cleaned Tenax was dried in a muffle furnace at 200°C for 24 hours, and then stored in methanol for later use. Before use, it was put into a glass tube and dried at 200°C for 4 hours, cooled down to room temperature in the desiccator. The specific steps are as follows: Take 2 g soil sample that adsorbs the target pollutants phenanthrene and pyrene, and then put it into a 15 ml Teflon centrifuge tube with septa, add 14 ml deionized water, add 0.2 g Tenax ball, vibrate and desorb it in a shaker at a constant temperature ($22\pm 1^\circ\text{C}$) in dark, and take out the centrifuge tube at 5 min, 30 min, 1 h, 6 h, 24 h, 48 h, 72 h, 168 h, 480 h, 720 h to analyze the contaminant samples contained in the Tenax ball. Tenax ball has great adsorption capacity, so it can be considered that the concentration of pollutants in the liquid phase is extremely low. Previous studies have found that the recovery rate of PAHs adsorbed by Tenax ball is above 98%. Therefore, it can be considered that the concentration of pollutants in the Tenax ball is the desorption amount of soil adsorbed PAHs by water phase [28].

Extraction and Determination of PAHs

Concentrations of phenanthrene and pyrene in soil samples and earthworm samples were determined using accelerated solvent extraction

(ASE). Specifically, 1 g sample was mixed with 4 g diatomaceous earth and then put into ASE extraction container. Under acetone/n-hexane (volume ratio 1:1), temperature 125°C , pressure 10 MPa, perform preheating and static extraction 5 min each, and repeat 2 times. The solvent flushing volume is 60% volume of the extraction vessel. Concentrate 2 ml of the extract and the previous mixed extract on a rotary evaporator and transfer it to a solid phase extraction column (SPE) (1g neutral Al_2O_3 +1 g silica gel + 1 g anhydrous sodium sulfate) for purification, and rinse with 25 ml n-hexane/dichloromethane (volume ratio 9:1). Collect the filtrate, concentrate to about 1ml, blow it dry with nitrogen, dilute the volume of acetonitrile to 1ml, pass through a $0.45\ \mu\text{m}$ organic filter membrane and use ultra-performance liquid chromatography (UPLC 1290) to determine the concentration. For extraction of PAHs in Tenax: Transfer the Tenax reaction system to a separatory funnel. Since Tenax has a lower density than water, it is easy to separate Tenax floating in the upper layer. After washing twice with Mili-Q water, use 15 ml n-hexane/ acetone (volume ratio 3:1) for three times' ultrasonic extraction. The three extracts were mixed, purified, and the concentration of PAHs was determined by ultra-high-performance liquid chromatography after constant volume.

UPLC determination method is as follows: for pollutants, use UPLC, detection array DAD detector and FLD detector with diode tube to pre-establish $0.1\sim 1000\ \text{mg}\cdot\text{L}^{-1}$ concentration range of phenanthrene and pyrene standard curve. UPLC measurement conditions are as follows: the mobile phase is acetonitrile and Mili-Q water, the volume ratio is 78:22; the flow rate is $0.4\ \text{mL}\cdot\text{min}^{-1}$, the column temperature is 35°C , the injection volume is $15\ \mu\text{L}$, and the detection wavelength of the DAD detector is $254\ \text{nm}$, the peak time is 1.9 min. For pyrene, mobile phase acetonitrile and Mili-Q water, volume ratio 68:32; flow rate $0.6\ \text{mL}\cdot\text{min}^{-1}$, column temperature 35°C , injection volume $8\ \mu\text{L}$, FLD detector excitation wavelength $270\ \text{nm}$, emission wavelength $392\ \text{nm}$, appearance time 2.5 min.

Biological Accumulation Kinetics Experiment on Earthworm

Pretreat adult earthworms (*Eisenia fetida*) with the same mass (0.5 g) (incubate for 20 d in the dark in the incubator, control the temperature at $28\pm 1^\circ\text{C}$, and add Mili-Q water twice a day to ensure that the soil moisture is around 50%). For each group, randomly select 3 pieces and put them into 200 ml brown glass bottles, add 200 g soil containing PAHs, randomly take out one group respectively at 0.5 d, 1 d, 3 d, 5 d, 10 d, 15 d, 20 d, 30 d to analyze the kinetic accumulation concentration of earthworms. Wash the surface with deionized water, clean the stomach and intestines for 48 h, freeze-dry and grind. After grinding, ASE was extracted, and the PAH concentration was analyzed by

UPLC to determine the bioavailability concentration of PAHs in the soil at different time points. According to the pre-experimental results, the earthworms reach the equilibrium concentration in the body within 15 d. In order to ensure the experimental accuracy, this study selected 30 d as the end point of bioavailability accumulation in the earthworms.

Data Processing and Quality Assurances

The experimental data of desorption rate was fitted using a classic first-order binomial model (Eq. 3) [24, 29, 30]. The bioavailability of PAHs was calculated using Jager T's earthworm-soil accumulation factor (Eq. 4) [31].

$$S_t/S_0 = F_{rap} \times e^{(-k_{rap} \times t)} + F_{slow} \times e^{(-k_{slow} \times t)} \quad (3)$$

Where, S_t and S_0 ($\text{mg} \cdot \text{kg}^{-1}$) are the concentrations of pollutants on the solid phase at the time of desorption t and the initial reaction. The greater the S_t/S_0 , the smaller the degree of desorption and the more difficult the desorption. F_{rap} and F_{slow} (%) are fast and slow desorption components; k_{rap} and k_{slow} (h^{-1}) are rate constants.

$$\text{Earthworm-soil accumulation factor ESAF} = \frac{C_e(t)}{C_s(0)} \quad (4)$$

Where: ESAF is the earthworm bioaccumulation factor; $C_e(t)$ is the pollutant concentration in the earthworm at time t , $\text{mg} \cdot \text{kg}^{-1}$ fresh weight; $C_s(t)$ is the pollutant concentration in the soil at time t , $\text{mg} \cdot \text{kg}^{-1}$.

All experiments were set up with 3 parallel samples, and a blank control group was set up; interval addition method was used for determination during the high-performance liquid chromatography analysis. For the experimental results, use SPSS24.0 to perform one-way ANOVA and correlation analysis on the data, and use OriginPro 2021b and CorelDRAW.X8 for graphic plotting.

Results and Analysis

Recovery Rate of PAHs in Soil Extracted by ASE

The results of initial pollutant concentration in the soil extracted by ASE showed that the recovery rates of phenanthrene and pyrene in the four types of soils were all above 95% (Fig. 2). The concentration of pollutant phenanthrene under different rocky desertification grades is 48.0 mg/kg - 50.57 mg/kg , the pollution concentration of PAHs pyrene is 48.53 mg/kg - 51.47 mg/kg , and the relative standard deviations are all within 10%. The experiment can effectively avoid the influence of external factors (such as reaction flasks, laboratory working environment,

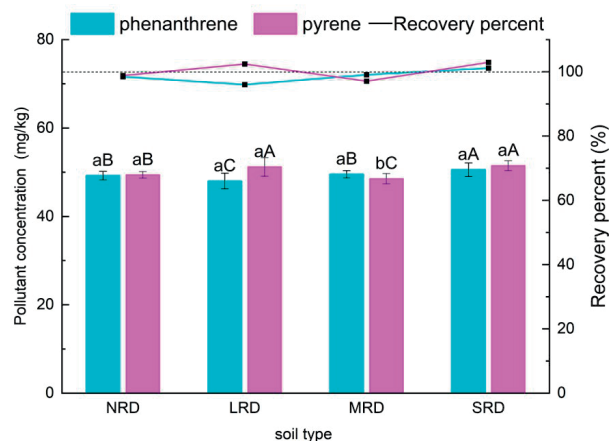


Fig. 2. Dichloromethane extracts the adsorption concentration of lime soil of different rocky desertification grades. (Note: the letters in the figure represent the significant differences of the same type of pollutants in different soils, lowercase letters are $P < 0.05$; uppercase letters are $P < 0.01$).

etc.). In a short aging time, the ASE exhaustive organic solvent extraction method can maximally extract the pollutants in various existing states (organic bound state, water dissolved state, residual state, and organic acid dissolved state) in the soil, so in this experiment, 50 mg/L phenanthrene and pyrene added in the soil can be used as the initial concentration for pollutant migration and transformation.

Desorption Kinetics of PAHs in Different Rocky Desertification Soils

The study results showed that the desorption kinetic behavior in the soil with different rocky desertification grades changes significantly. With the increase of rocky desertification intensity, the fraction of rapid desorption of pollutants phenanthrene and pyrene increase, the fast desorption rate increases, and the degree of desorption increases. The concentration of pollutants in the solid phase is reduced. The results reveal that the equilibrium time for desorption concentration of phenanthrene and pyrene is approximately 7 d (Fig. 3) and the concentration of residual or fixed pollutants in the soil decreases. From the S_t/S_0 data of pollutant residual rate, it can be seen that the residual rate of pollutant phenanthrene and pyrene gradually decreases from 37% and 60% in the non-rocky desertification soil to 22% and 38% in the severe rocky desertification soil, a decrease of 25% and 22%, respectively. The first-order binomial fitting data shows (Table 2) that with the increase of rocky desertification grade, the fraction of rapid desorption (F_{rap}) values of pollutants phenanthrene and pyrene in the soil increase from 54.58% and 35.19% in the non-rocky desertification soil to 73.09% and 50.98% in the severe rocky desertification soil, with changes of 18.51% and 15.19%, respectively. The fraction of rapid desorption and the

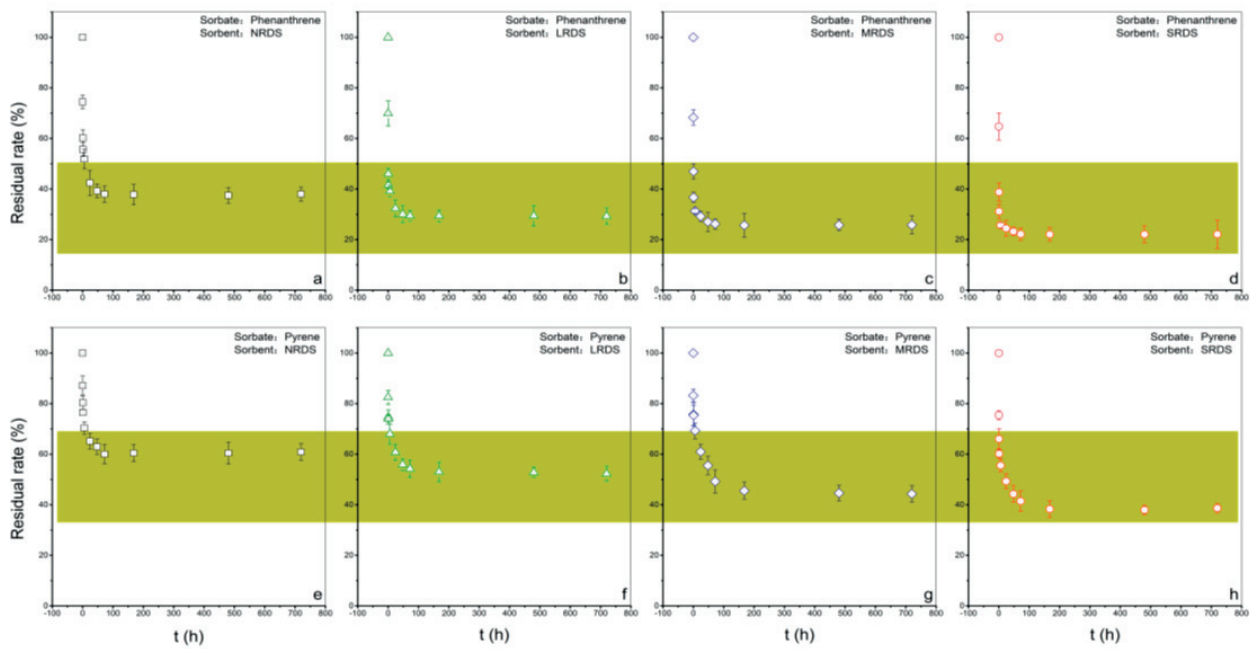


Fig. 3. Desorption kinetics diagram of phenanthrene and pyrene in different types of soils. (residual rate corresponds to the ratio of St/S_0 ; (a-d) diagrams show desorption rates of phenanthrene in non-rocky desertification, light rocky desertification, moderate rocky desertification and severe rocky desertification soils; e-h diagrams show the desorption rates of pyrene in non-rocky desertification, light rocky desertification, moderate rocky desertification and severe rocky desertification soils; the shaded part in the figure shows the concentration range under equilibrium desorption of phenanthrene and pyrene in different rocky desertification soils).

change range of phenanthrene in the same soil type are higher than those of the pollutant pyrene, which may be related to the hydrophobicity of the pollutant. Studies have shown that more hydrophobic PAHs are more likely to be adsorbed by soil particles, and the adsorption energy is significantly higher than the less hydrophobic PAHs [32, 33]. Except for the moderate rocky desertification soil, the rapid desorption rate (k_{rap}) of the pollutants phenanthrene and pyrene in the soil presents an increasing trend with the increase of rocky desertification grade. The k_{rap} of pollutant phenanthrene increased from 3.57 h^{-1} in non-rocky desertification soil to 6.89 h^{-1} in severe rocky desertification soil, an increase of 3.32 h^{-1} . The k_{rap} of pollutant pyrene increased from 1.51 in non-rocky desertification soil to 2.61 in severe rocky desertification soil, with a change range of 1.10 h^{-1} . The change range of

slow desorption rate of phenanthrene and pyrene is between $3.67 \times 10^{-4} \sim 4.03 \times 10^{-4}$ and $1.26 \times 10^{-4} \sim 4.78 \times 10^{-4}$, respectively. The fast and slow desorption rates are in the same order of magnitude as previous studies [34, 35]. In general, both the fast and slow desorption rates tend to increase with the increase in rocky soil desertification grade.

Results of Earthworm Biology Experiment

The study results showed that earthworms had very obvious PAHs accumulation in the four different similar soils, and as the degree of rocky desertification increased, the PAHs accumulation in earthworm body lipids gradually increased. It can be seen from Fig. 4 that during the 30d incubation of the earthworms, the concentrations of the pollutants phenanthrene

Table 2. Desorption rate parameter values of pollutants in soils of different rocky desertification grades.

Soil	Phenanthrene				Pyrene			
	F_{rap} (%)	k_{rap} (/h)	k_{slow} ($*10^{-4}/h$)	R^2	F_{rap} (%)	k_{rap} (/h)	k_{slow} ($*10^{-4}/h$)	R^2
NRDS	54.58(3.31) ^a	3.57(1.33)	3.67(2.67)	0.87	35.19(2.20)	1.51(0.42)	1.26(1.07)	0.89
LRDS	64.23(2.18)	6.49(1.58)	4.03(2.41)	0.95	39.51(3.18)	1.85 (0.69)	2.68(1.77)	0.83
MRDS	68.61(2.49)	5.16(1.32)	3.95(3.05)	0.94	40.72(3.94)	1.49(0.62)	5.51(2.52)	0.83
SRDS	73.09(1.96)	6.89(1.32)	3.99(2.88)	0.96	50.98(3.66)	2.61(0.97)	4.78(2.79)	0.86

Note: ^a is the standard error.

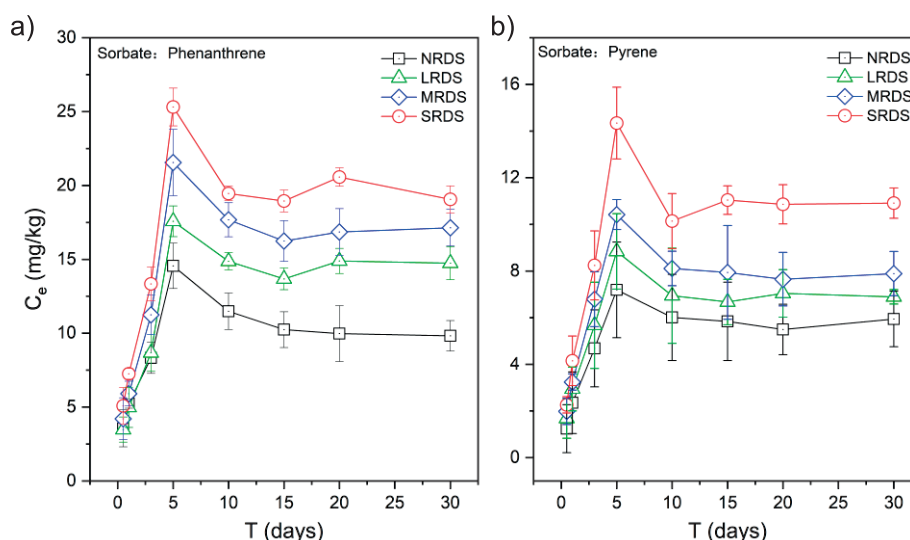


Fig. 4. The accumulation concentration of phenanthrene and pyrene in earthworms at different times under different rocky desert soils. a) represents the accumulation concentration of phenanthrene in earthworms; b) represents the accumulation concentration of pyrene in earthworms; NRDS is non-rocky desertification soil; LRDS is light rocky desertification soil; MRDS is moderate rocky desertification soil; SRDS is severe rocky desertification soil.

and pyrene in the earthworms under different rocky desertification soils tend to first increase and then decrease, reaching the highest accumulation value in 5 d and basically reaching concentration equilibrium in the body within 10 d. The peak concentrations of phenanthrene and pyrene in the four different types of rocky desertification soils are as follows: 14.56 mg/kg and 7.19 mg/kg in non-rocky desertification, 17.58 mg/kg and 8.84 mg/kg in light rocky desertification, 21.55 mg/kg and 10.42 mg/kg in moderate rocky desertification, 23.31 mg/kg and 14.34 mg/kg in severe rocky desertification. The data in Table 3 shows that after 30 d incubation, the equilibrium concentrations of phenanthrene and pyrene accumulated in earthworms are 9.82 mg/kg and 5.94 mg/kg in non-rocky desertification soil, 14.74 mg/kg and 6.89 mg/kg in light rocky desertification soil, 17.14 mg/kg and 7.89 mg/kg in moderate rocky desertification soil, 19.06 mg/kg and

10.91 mg/kg in severe rocky desertification soil. For this reason, in the early period, earthworms absorb large amounts of phenanthrene and pyrene from the soil in a relatively short period of time. When the concentration reaches the maximum, the increased metabolism and absorption of earthworms produces a counteract effect, which leads to decreased concentration of pollutants in the body, followed by a balance between metabolism and absorption, so accumulated concentration of earthworms reaches equilibrium.

In different periods of earthworm cultivation, PAHs phenanthrene and pyrene have different change ranges in different rocky desert soils, showing unobvious regularity. The study results showed that in the case of phenanthrene, the accumulation rate of pollutants in earthworms increased before 5 d, and the accumulation rate in earthworms was less obvious in light rocky desertification soils than in non-rocky

Table 3. Experimental results of earthworm accumulation equilibrium in different rocky desertification soils.

Sample	Phenanthrene			Pyrene		
	C_e (mg/kg)	R_{ac} (%)	ESAF	C_e (mg/kg)	R_{ac} (%)	ESAF
NRDS	9.82	19.95	0.25	5.94	12.02	0.14
LRDS	14.74	30.71	0.44	6.89	13.46	0.16
MRDS	17.14	34.61	0.53	7.89	16.26	0.19
SRDS	19.06	37.69	0.60	10.91	21.19	0.27

Note: C_e is the body concentration of earthworms under accumulation equilibrium; R_{ac} is the concentration accumulation rate in earthworms body, $R_{ac} = C_e/C_0$, C_0 is the initial concentration in soil; ESAF is the accumulation factor of earthworm bioavailability.

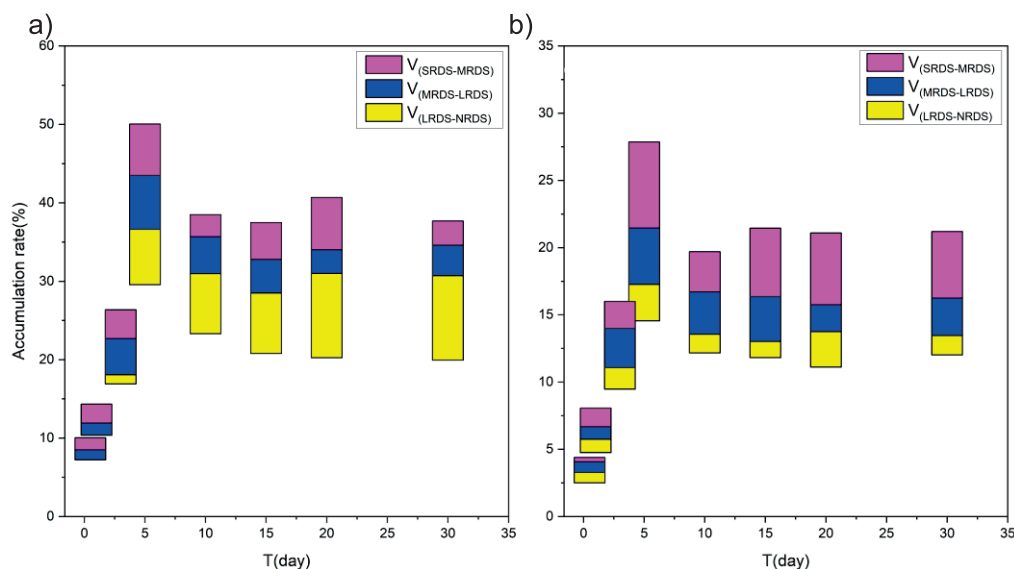


Fig. 5. The change range of the concentration of phenanthrene and pyrene in earthworms under different rocky desertification soils. (a represents phenanthrene; b represents pyrene; $(V_{LRDS-NRDS})$ represents the difference in the concentration change of pollutants accumulated by earthworms in LRDS and NRDS; $(V_{MRDS-LRDS})$ represents the difference in the concentration change of the pollutants accumulated by the earthworms in the MRDS and LRDS; $(V_{SRDS-MRDS})$ represents the difference in the concentration changes of pollutants accumulated by earthworms in SRDS and MRDS).

desertification soils ($V_{LRDS-NRDS}$), with change range of -0.08 — $+0.34$. Moderate rocky desertification soil and light rocky desertification soil ($V_{MRDS-LRDS}$) have more obvious change than severe rocky desertification soil and moderate rocky desertification soil ($V_{SRDS-MRDS}$), with change range of $+0.73$ — $+2.57$ and $+0.87$ — $+2.10$, respectively. After 5 d peak value accumulation, $V_{LRDS-NRDS}$, $V_{MRDS-LRDS}$ and $V_{SRDS-MRDS}$ change in the range of $+3.02$ — $+4.92$, $+1.96$ — $+3.97$ and $+1.76$ — $+3.72$, with obvious change range. For the more hydrophobic pyrene, the pollutant accumulation in earthworms rises in the first 5 d, $V_{LRDS-NRDS}$, $V_{MRDS-LRDS}$ and $V_{SRDS-MRDS}$ show no obvious changes, with changes in the range of $+0.44$ — $+0.99$, $+0.30$ — $+1.12$ and $+0.28$ — $+1.45$, respectively. After peak accumulation on 5d, $V_{LRDS-NRDS}$, $V_{MRDS-LRDS}$ and $V_{SRDS-MRDS}$ change in the range of $+0.83$ — $+1.65$, $+0.61$ — $+1.58$ and $+2.03$ — $+3.92$ with significant change ranges (Fig. 5). Therefore, the author believes that in the early stage of pollutant accumulation by earthworms, changes in rocky desertification soil characteristics are the main reason that affects the PAHs accumulation in earthworms. After the pollutants in the earthworms reach the peaks, under the effect of metabolism, the soil type or rocky desertification soil characteristics produce insignificant effect on PAHs accumulation in earthworms. The overall trend is that phenanthrene with low ring, low hydrophobicity creates bigger effect than pyrene with high ring, high hydrophobicity.

The migration and transformation results of phenanthrene and pyrene concentration in different rocky desertification soils show that regardless of phenanthrene or pyrene, the bioavailability components usable by earthworms present an increasing trend in different rocky desertification soils (Fig. 6).

The pollutants of fraction of rapid desorption in the soil are the part preferentially used by organisms and also first released from the soil matrix. From the data in the figure, it can be found that among the four types of soils, the fraction of rapid desorptions of phenanthrene and pyrene account for 45.00%, 52.00%, 55.00% and 62.00% respectively. The occurrence state of PAHs in the soil shows that 49.50%, 41.00%, 34.50% and 30.00% of the four types of soils are isolated or "aging" pollutants, 34.50%, 37.50%, 40.50% and 40.50% are free pollutants, 16.00%, 21.50%, 25.00% and 29.50% are bioavailable pollutant components. In terms of different pollutants, the proportions of phenanthrene bioavailability components in soil from non-rocky desertification soil to severe rocky desertification soil are 20.00%, 30.00%, 34.00% and 38.00%, respectively; the proportions of pyrene bioavailability components in soil from non-rocky desertification to severe rocky desertification soil are 12.00%, 13.00%, 16.00% and 21.00%, respectively.

Discussion

The Impact of Different Rocky Desertification Soil Properties on the Desorption of PAHs

Physical and chemical properties of soil as a pool of PAHs determine the environmental behavior of PAHs adsorption. Tenax desorption results show that with the increase of rocky desertification intensity, desorption capacity of phenanthrene and pyrene in the soil increases, and so is the equilibrium desorption concentration. With the increase of rocky desertification

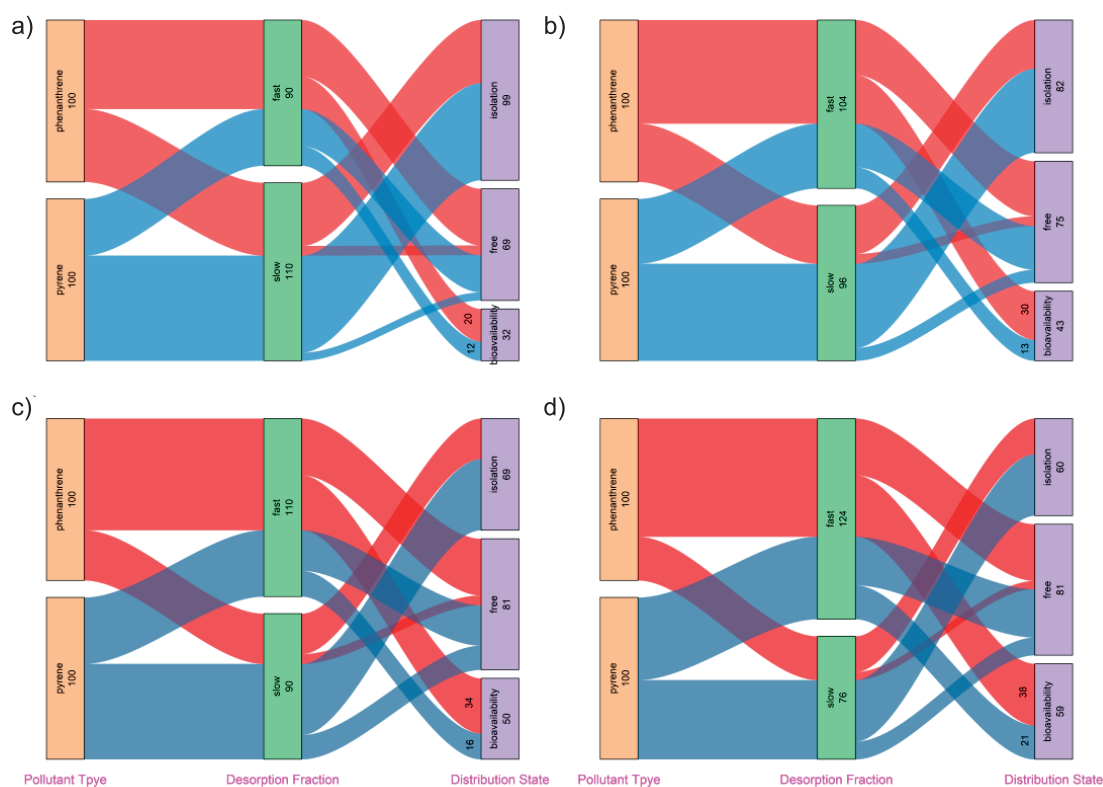


Fig. 6. Migration paths of phenanthrene and pyrene bioavailability components in different types of rocky desertification soils. a) represents non-rocky desertification soil; b) represents light rocky desertification soil; c) represents moderate rocky desertification soil; d) represents severe rocky desertification soil.

intensity, the fraction of rapid desorption of PAHs in the soil increase, and both the fast and slow desorption rates tend to increase. This indicates that different rocky desertification soils change the desorption kinetics of PAHs and also suggests that rocky desertification soil characteristics significantly affect the migration, occurrence and transformation of PAHs. Regardless of phenanthrene or pyrene, the increase in fraction of rapid desorption and the increase of equilibrium desorption amount indicates that the soil's ability to hold pollutants is weakened. Existing studies show that fraction of rapid desorption in soil are mainly physically distributed pollutants in soil, while slow desorption components are mainly pollutants dominated by strong chemical adsorption [36, 37]. Seen from the perspective of Pearson correlation (Fig. 7) and RDA (Fig. 8), the physical and chemical properties of soils of different rocky desertification types have certain correlations. The fraction of rapid desorption of the pollutants phenanthrene and pyrene have a significant negative correlation with soil organic carbon, and a significant positive correlation with soil water-soluble calcium content. Therefore, analyzed from soil properties, the desorption capacity of PAHs in the soil is highly correlated with factors such as organic carbon, water-soluble calcium content, base saturation, porosity, and specific surface area. RDA analysis shows that soil organic carbon, base saturation, and pore volume

can explain 98.00% of the desorption behavior of phenanthrene and pyrene in soil and the accumulation of bioavailability factors, while soil pore volume and base saturation account for 58.30%. Numerous studies have shown that soil organic carbon plays a decisive role in the environmental behavior of organic pollutants in soil. The higher the organic carbon content, the stronger the holding capacity against PAHs [38, 39]. Due to the unreasonable use of land and unique environmental conditions in the southwestern karst rocky desertification area, the ecological environment fragility is significantly higher compared to non-rocky desertification area. Studies have shown that with the increase of rocky desertification, the physical and chemical properties of the soil change significantly, the soil organic matter is significantly reduced, and the soil thickness is significantly reduced. The reduction in soil thickness is also unconducive to the preservation of soil organic matter. At the same time, karst rocky desertification areas have less overlying vegetation on soil, which is also unfavorable for the formation of soil organic matter [40], while soil organic matter is a key factor affecting the adsorption and desorption of soil PAHs. The specific surface area of soil is mainly the specific surface area of soil mineral particles and organic matter. PAHs combines with soil mainly through distribution, electrostatic interaction, hydrogen bonding, and π - π bonding [13, 32, 41]. Studies have

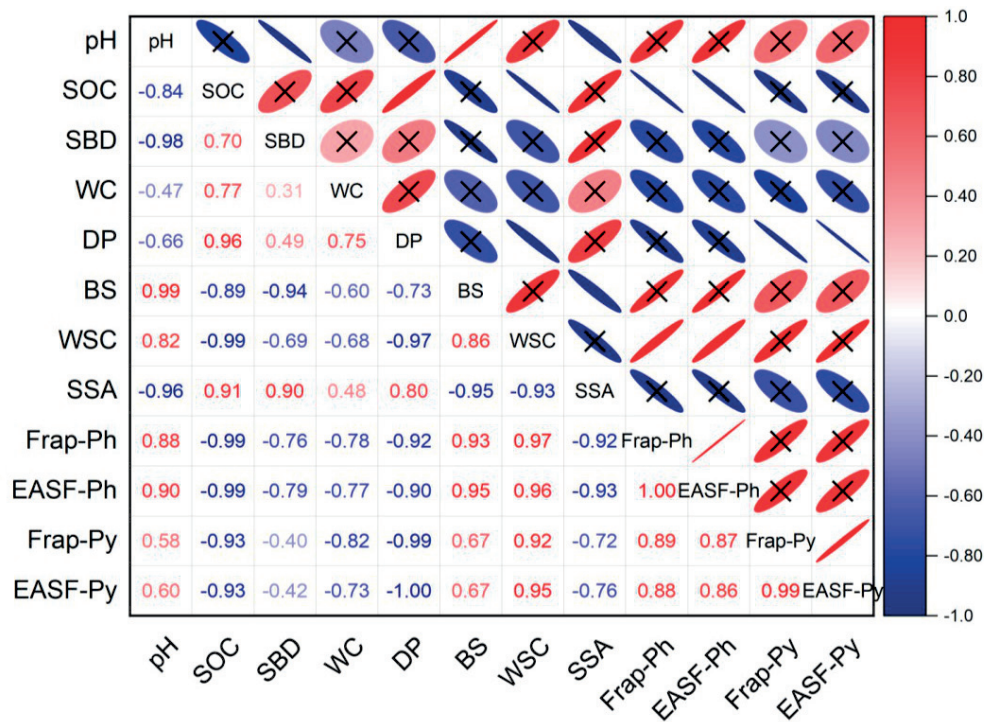


Fig. 7. Pearson analysis of phenanthrene and pyrene fraction of rapid desorption, earthworm bioaccumulation factors and soil physical and chemical properties. (the significance level is $p < 0.05$; X represents the significance level $p > 0.05$; F_{rap} -Ph represents the fast desorption component of phenanthrene in the soil; F_{rap} -Py represents the fast desorption component of pyrene in the soil).

shown that the larger the specific surface area, the more the chemically strong adsorption sites of PAHs, the easier it is for pollutants to be trapped in the soil environment [42, 43]. Our research shows that the specific surface area of the soil is the main factor that controls the migration behavior of PAHs in rocky desertification areas. Since the initial concentrations in soils of different rocky desertification grades are

basically the same, the adsorbed pollutants in the soil with reduced specific surface area are mainly pollutant molecules physically distributed to the soil. Therefore, during desorption, the concentration of pollutants in the solid phase of the soil decreases greatly, which is manifested by the enhanced desorption capacity and the smaller soil binding effect.

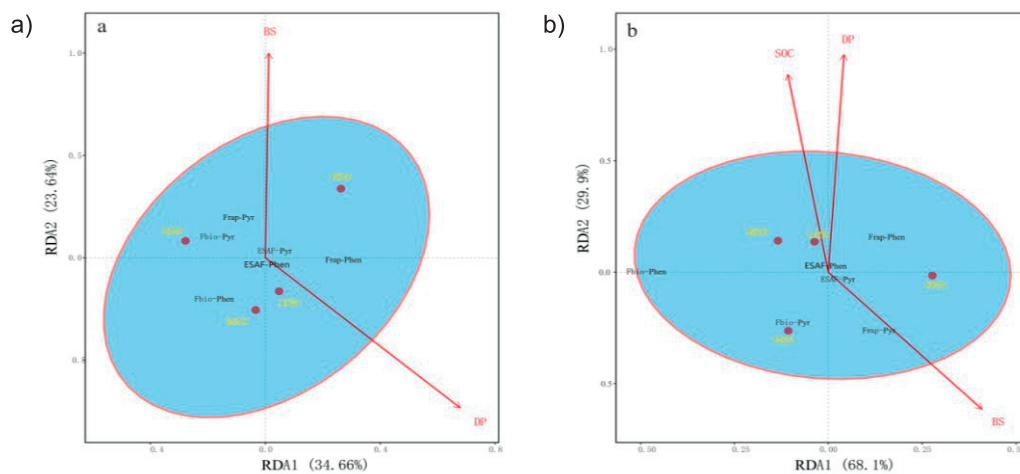


Fig. 8. RDA analysis of phenanthrene and pyrene fraction of rapid desorption, earthworm bioaccumulation factors and soil physical and chemical properties. (ESAF-Ph represents the bioaccumulation factor of phenanthrene in earthworms; ESAF-Py represents the bioaccumulation factor of pyrene in earthworms. a) is the dual environmental factor RDA; b) is the three environmental factors RDA; SOC is soil organic carbon; DP is pore volume; BS is base saturation; F_{bio} -Ph is the bioavailability component of phenanthrene; F_{bio} -Py is the bioavailability component of pyrene).

Soil properties indicate that the porosity decreases with the increase of rocky desertification, and soil pores, especially micropores, have much greater binding effect on organic molecules than macropores and mesopores. Xing Baoshan's team believed that the desorption hysteresis of PAHs in the soil is mainly related to the micropore filling mechanism. As the aging time of soil pollutants increases, PAHs molecules will gradually migrate to the depths of the pores, thus difficult to release during desorption [44-46]. Research suggests that the decline in porosity of karst rocky desertification soil in Southwest China has certain impact on the environmental behavior of PAHs. As the degree of rocky desertification increases, soil porosity decreases, and pollutant molecules entering micropores or micropores depth are smaller and fast released during desorption, with fast desorption component increased. Our previous studies have also shown that natural environmental processes will change the structure of PAHs adsorbed by soil, and the microporous structure will also change. Southwestern karst soil has undergone different natural environmental processes, and the physical structure of the soil will change. Therefore, the author believes that the rocky desertification environment in southwestern karst soil will affect the desorption behavior of soil PAHs by changing the number and structure of micropores.

The Effect of Calcium-Rich Karst Rocky Desertification Soil on Desorption Behavior

In different rocky desertification areas, the type and strength of ions in the desorption aqueous solution will affect the desorption of PAHs. The study results show that as the degree of rocky desertification increases, the

content of soluble calcium in the desorption solution increases, the desorption capacity of PAHs increases, and the concentration of pollutants contained in the solid phase of soil decreases. Previous studies believe that the desorption environment is the most significant factor that affects desorption and bioavailability of pollutants in addition to the physical and chemical properties of the soil and the nature of the pollutants. Previous studies have shown that desorption environments such as pH, ionic strength, freeze-thaw cycles, and dry-wet alternation all affect the adsorption and desorption behavior of organic pollutants [47-51]. The bedrock in the southwestern karst area produces a large amount of calcium-containing minerals during the process of weathering and soil formation, the soil base saturation will increase with the increase of rocky desertification, and high content of Ca^{2+} will be released in the aqueous system. The author believes that calcium-rich properties of soil in karst rocky desertification areas will affect the desorption and bioavailability of PAHs from four aspects (Fig. 9). First, the change of ionic strength will affect the change of surface potential of the variable charge surface. Under higher ionic strength, the absolute value of the variable charge surface potential will decrease, and the surface potential will decrease, resulting in decreased soil adsorption potential and weakened adsorption capacity. Second, at the same time, metal ions will form complex ions with water molecules and form a competitive effect with pollutant molecules, reducing the PAHs sites of soil adsorption. Third, the presence of metal ions will produce similar salting-out or salting-in effects. Under the salting-out effect, the solubility of pollutants in the solution will decrease, and pollutants at low-energy points tend to be desorbed and released, resulting in enhanced desorption

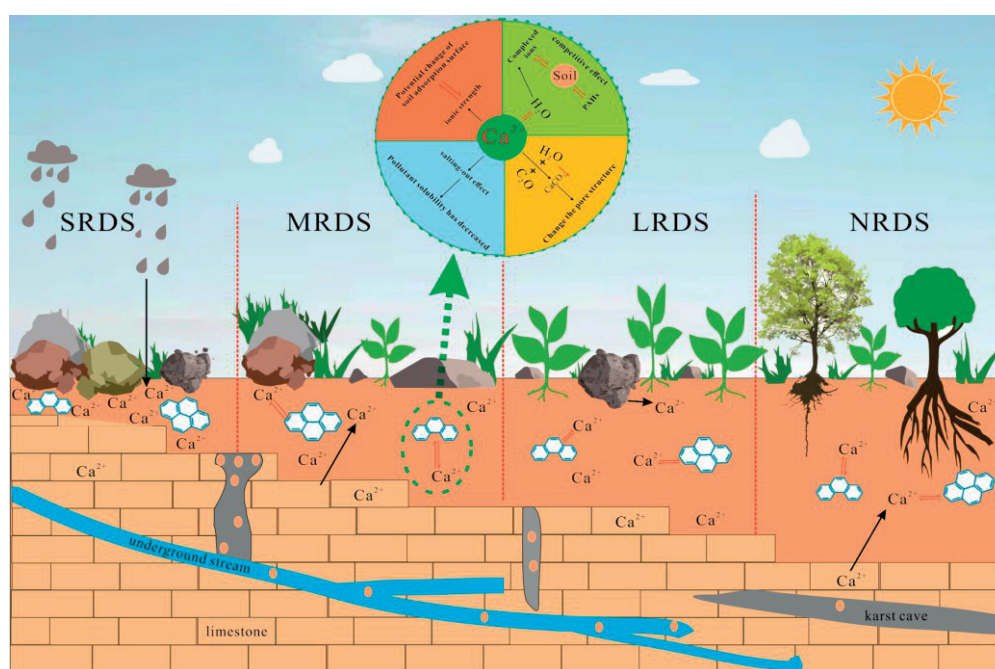


Fig. 9. Conceptual model of the desorption mechanism of calcium ions on PAHs in karst soils.

capacity. Fourth, calcium ions will form precipitates such as calcium carbonate under the action of the natural environment, change the microporous structure of the soil or block the pores, making it difficult for pollutant molecules to enter the microscopic pores. The pollutants are mainly distributed on the surface, the adsorbed pollutants are reduced, and the free state pollutant molecules increase, leading to increased desorption. This is consistent with the study by Oh et al. that the increase in salinity leads to a decrease in the desorption hysteresis index of PAHs in the soil, which may also be caused by the salt precipitation of metal ions and changes in the micropore structure [52]. Studies have pointed out that the softness of Na^+ and Ca^{2+} are -5.51 and -2.92, respectively, which are less than 0 and belong to hard acid metal ion [53]. According to Mulliken principle and Koopman closed-shell molecular theorem, the electronegativity of phenanthrene and pyrene is calculated as <2.8 , belonging to soft alkalis. According to the principle of "soft and hard affinity" in Pearson's soft and hard acid-base theory, the pollutants phenanthrene and pyrene and metal Ca^{2+} belong to different types of substances, so there is a repulsive effect, which promotes PAHs desorption in the soil [54]. Yuan and Xing pointed out that the addition of exogenous Ca^{2+} and Al^{3+} to humic acid will change its ability to adsorb and desorb PAHs [55]. The results show that Al-HA combination is more likely to incur desorption hysteresis, while Ca-HA desorption hysteresis is unobvious. Wang et al. believed that metal ions may block micropores and reduce the adsorption of nitrophenol on sediments [56]. Therefore, the study has reference value for the migration, transformation, fate and bioavailability of PAHs in the calcium-rich soil in the fragile karst ecological environment of Southwest China.

The Impact of Different Karst Rocky Desertification Soils on Bioavailability

The desorption amount of pollutants phenanthrene and pyrene in the soil with different rocky desertification

levels increased significantly, resulting in increased content of pollutants touched by the earthworms. Under the tolerance of the earthworms, the concentration of pollutants absorbed by the earthworms is bound to increase, leading to increased biological accumulation factor. The existing state of pollutants in the soil determines the bioavailability of PAHs in earthworms. Previous studies have suggested that isolated or aged PAHs are difficult to release into the water and soil system and will not be used by earthworms and other organisms, but in the process of rocky desertification evolution, whether these aging pollutants will be released as environmental conditions change is a scientific issue that needs further exploration. Other forms of PAHs in the soil are biologically accessible pollutants, but are not necessarily used by earthworms. In other words, they do not necessarily appear as bioavailable concentrations. Therefore, how to quickly determine the accurate concentration of organisms in the soil is crucial to assessment of the ecological risk of PAHs. Previous studies have suggested that the extraction concentration of Tenax 6h is significantly positively correlated with the bioavailability concentration [6, 57]. Our research found that the Tenax 1h extraction concentration in karst rocky desertification calcium-rich soil has a similar correlation with the accumulation equilibrium concentration of earthworm body as Tenax 6h. The author considers that the calcium ion content in rocky desertification soil accelerates the fast desorption concentration of PAHs in the soil, the extraction concentration of Tenax 1h in the soil of rocky desertification area and the bioavailability concentration in earthworms are closer to the equilibrium concentration of earthworm intake and metabolism. Different soil characteristics will affect the PAHs occurrence state in the soil. Therefore, when using Tenax extraction concentration as a bioavailability concentration indicator, the specific characteristics of the soil should be considered, especially the soil type in a special environment. Semple et al. [58] and Luo et al. [59] also found that toxic compounds are not only related to the nature of pollutants, but also closely

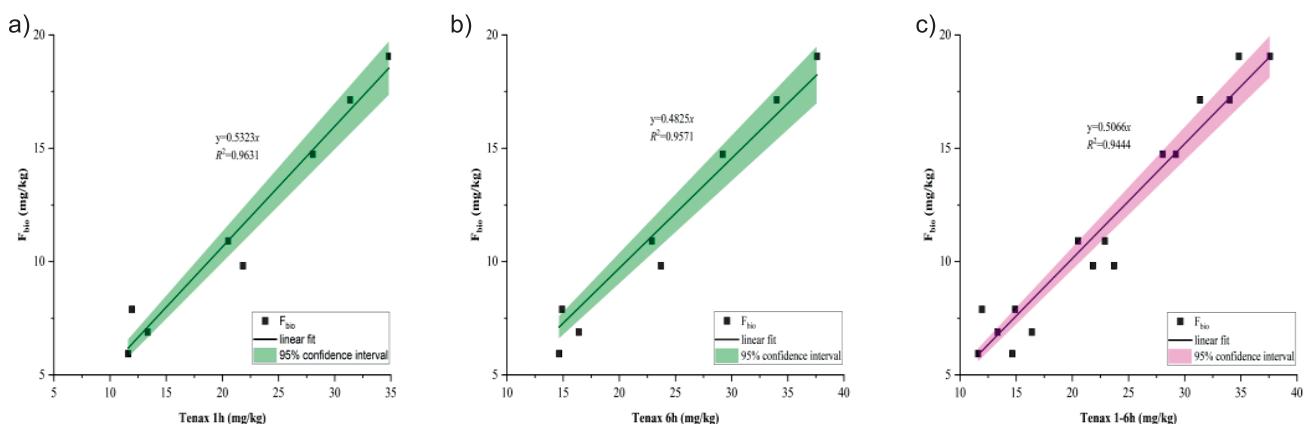


Fig. 10. The relationship between Tenax 1-6 h extract concentration and bioavailability components.

related to the physical and chemical properties of the soil and the ingestion way of earthworms. The results of this study show (Fig. 10) that the bioavailability fractions (F_{bio}) of PAHs in karst rocky desertification soil is about twice the concentration of Tenax 1h-6h, so the extraction concentration of Tenax 1-6h can be used as a quick judgment criterion.

Conclusion

The migration, transformation and bioavailability of PAHs in karst rocky desertification areas have an important impact on the risk assessment of PAHs-contaminated soil in a fragile ecological environment. The unique calcium-rich characteristics of soil in rocky desertification areas are important factors affecting the desorption and bioavailability of PAHs. The study found that: (1) The desorption of PAHs in soils in the southwest karst area is related to the level of rocky desertification in the soil. The higher the level of rocky desertification, the easier the desorption. (2) Pearson and RDA analysis shows that soil organic carbon, base saturation, and porosity are the main physical and chemical properties that affect the physical and chemical properties of Southwestern Karst soils, which affect the desorption capacity and bioavailability accumulation factors of phenanthrene and pyrene. (3) The increase of calcium ion content in soil in karst rocky desertification area may promote the desorption of PAHs and increase its bioavailability. Compared with NRDS, the fraction of rapid desorption of phenanthrene in SRDS, MRDS and LRDS are increased by 18.51%, 14.03% and 9.65%, respectively; those of pyrene are increased by 15.79%, 5.53% and 4.32%, respectively. (4) The bioavailability component F_{bio} of PAHs in karst rocky desertification areas is about twice that of Tenax 1-6h extraction components, so Tenax 1-6h extraction components can be used as effective surrogate markers for PAHs-contaminated soil.

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Conflicts of Interest

The authors declare no conflict of interest.

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