Catena 225 (2023) 107026

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Soil nitrogen transformation in different land use and implications for karst soil nitrogen loss controlling

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ARTICLE INFO

Keywords:
Karst
Soil profile
Land use
Nitrogen content
Nitrogen isotope

ABSTRACT

A large amount of cropland in the Southwestern (SW) China karst area has been abandoned since the implementation of the Grain for Green project at the end of the last century, which significantly impacted the biogeochemistry cycle in soil. However, the effect of cropland abandonment on the soil nitrogen (N) cycle and the N loss process is still little understood. N content and isotope analysis were used to assess karst soil's N fate and explore the N loss process in SW China. Soil samples were collected from four land uses, cropland (CR), abandoned CR (AC), shrubland and grassland (SG), and secondary forest (SF), by seasonal in a typically mixed land-use karst catchment at six soil depths. The results showed that the average soil particulate organic N (PON) content increased from 1.58 ± 0.49 g kg^{-1} to 2.70 ± 1.82 g kg^{-1}, whereas average dissolved nitrate (NO_3^--N) content decreased from 10.77 ± 8.87 mg kg^{-1} to 1.72 ± 1.84 mg kg^{-1} during revegetation. There was a decreasing amount of PON and dissolved N (NH_4^+-N、NO_3^--N、TDN) content from surface to the bottom of the soil profile and large variation mainly occurred in 0 – 30 cm in the soil profiles of four different land uses, which suggests N transformation mainly occurred in topsoil (<30 cm). Mineralization was the major nitrogen transformation process that affected PON content and δ^{15}N-PON values. The highest δ^{15}N-PON fractionation (-5.0‰) in the soil profiles of the four types of land use caused by mineralization was detected in SF. Variation of N content and isotope values in soil profiles after cropland abandonment suggested that the loss of NO_3^--N in karst catchment mainly came from the topsoil of cropland. Overall, N loss from the topsoil of cropland should pay more attention, while cropland abandonment can effectively reduce the loss of dissolved N from the thin karst soil layer.

1. Introduction

As a life support system and the central interface of Earth's critical zone (Chorover et al., 2007), soil plays a vital role in the biogeochemistry cycle (e.g., carbon and nitrogen) (Zhang et al., 2015; Jilling et al., 2018). Nitrogen (N) is one of the essential nutrients in terrestrial ecosystems to constrain plant growth and soil fertility (Amundson et al., 2003). Normally, organic N dominates the N stocks of soil and is influenced by abiotic factors, e.g., soil moisture, land use, and biotic factors, e.g., vegetation and microbial communities (Ramesh et al., 2019). The bioavailable forms of N in the soil, e.g., inorganic N and some low-molecular-weight organic N compounds (urea, amino acids, etc.), can constrain biomass production in either agriculture or forestry (Chapagain and Riseman, 2015; Ramesh et al., 2019). Previous studies focused on the transformation and potential driving factors between inorganic and organic N in soil systems of single land use, such as forest or farmland (Chen et al., 2012; Congreves et al., 2017; Song et al., 2019). In recent years, the impact of land-use change on the soil N cycle and the corresponding microbial communities has attracted scientific attention (Hu et al., 2016; Li et al., 2018a; Soldatova et al., 2021). However, there

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https://doi.org/10.1016/j.catena.2023.107026
Received 16 October 2022; Received in revised form 9 February 2023; Accepted 16 February 2023
Available online 21 February 2023

is a limited understanding of the N dynamic and its transformation processes in soil profiles with land-use change.

The expansion of the population has led to a marked change in land use over the last century due to unsustainable agricultural development (Foley et al., 2011; Zhang et al., 2015). For example, grassland and forest have degenerated into cultivated land in many places in China over the past century (Liu et al., 2010). Fortunately, the government initiated ecological engineering projects (e.g., Green for Grain, Mountain Closure, and Environmental Migration) to reduce soil erosion and improve the eco-environmental quality. Nowadays, cropland abandonment impacted the soil nutrient cycle and the surrounding water quality, especially influencing the soil N stocks and their biogeochemistry process (Li et al., 2017; Yang et al., 2020b). Synthetic N, such as chemical fertilizers, is the primary source of N in cropland (CR) (Clough et al., 2013; Sebilo et al., 2013), whereas N from the decomposition of organic matter constitutes the primary soil N source in other types of land use (Binkley et al., 2000; Hyodo and Wardle 2009). Identifying N sources and the transformation process in the soil profiles under various land use may help to understand the potential soil N loss process during the land conversion process after CR abandonment, especially in fragile karst areas that are easily degraded after extensive cultivation owing to the thin soil layer.

The karst landscape in China accounts for 13.5% of the total land area and is mainly distributed in the southwest, located in the center of one of three globally continuous larger karst areas (Jiang et al., 2014; Wang et al., 2019; Zhang et al., 2021). Approximately 30% of the mountain areas in Guizhou Province, the center of the Southwest China karst area, have slopes ranging from 17° to 25°, and 35% have slopes >25° (Peng and Wang, 2012). In extreme rainfall events, nutrient loss and soil erosion would degrade the karst ecosystem service, making it difficult to regenerate the vegetation and thereby accelerating rocky desertification (Borrelli et al., 2020; Li et al., 2021; Peng et al., 2019). Additionally, N loss from karst catchment has elevated nitrate export and subsequently resulted in nitrate concentration exceeding the threshold of drinking water in Chinese (GB3838-2002) (Wang et al., 2020; Yue et al., 2023). Thus, it is critical to identify the N fate based on the spatial and temporal in karst soils, which will be enhanced to understand the N loss under land-use change.

Previous studies have found that land use has impacted karst soil carbon stocks with vegetation restoration (Qin et al., 2022). Meanwhile, the stored N loss from CR soil was the major issue for the high N concentration in agricultural karst rivers (Wang et al., 2022b; Yue et al., 2020). The variation of N content and isotope values at different soil depths can understand the impact of land-use changes on the soil N cycle and also provide critical information on the soil N loss process, such as the affecting depths and loss species (Stevenson et al., 2010). However, the vertical variation of soil N content and isotope values in karst soil profiles of different types of land use after CR abandonment was still poorly understood. Generally, CR abandonment land would change from shrub and grassland, and subsequently, evolve into forest (Shen et al., 2020). Meanwhile, the biological mass may increase and enhance organic N stock accumulation (Smith et al., 2016; Aryal et al., 2018), while inorganic nitrogen may decrease owing to the decrease of chemical fertilizers input. Therefore, it can be hypothesized that dissolved nitrate content will decrease after CR abandonment, while PON content will increase, which may enhance to reduce soil N loss to the surrounding water bodies.

To explore the authenticity of this hypothesis, soil samples at six different depths surface (0–5 cm), 10 cm, 20 cm, 30 cm, 50 cm, and 70 cm were collected from four land-use profiles in a karst catchment during different agricultural periods. Soil particulate organic N (PON), dissolved N (NO_3^-、NH_4^+、TDN), the isotopic composition of soil organic N (δ^{15}N-PON) and dissolved nitrate (δ^{15}N-NO_3^-) were analyzed. The objectives were 1) to understand the change of soil N content in karst soil during revegetation, 2) to identify the N transformation in karst soil after CR is abandoned, and 3) to explore how the soil N cycle in different land-use contexts link to N loss in a karst catchment. The results would help to understand the N biogeochemical behaviors in the soil during the evolution of land use change.

2. Materials and methods

2.1. Study area

The Chenqi catchment (26°15′20′'–26°16′9′'N, 105°46′3′'–105°46′50′'E), with a surface area of 1.2 km^2 (Fig. 1), is located in a subtropical monsoonal climate zone with distinct dry and wet seasons based on Ambreje classification. The annual precipitation was 732 mm to 1770 mm between 2008 and 2017, with an average value of 1218 mm (Wang et al., 2022a). Approximately 86% of the annual rainfall occurs in the wet season (May to October). The average air temperatures in the wet and dry seasons of 2017 were 21.3 °C and 11.2 °C, respectively (Qin et al., 2022).

The surface elevation of the Chenqi catchment decreases from 1514 m to 1310 m above sea level. The calcareous soils are developed from limestone, with an average thickness of 64 cm (Chen et al., 2018). The higher elevations of surrounding hills are covered by forest (e.g., deciduous broad-leaved trees), shrubs (e.g., deciduous broad-leaved shrubs), and grass (e.g., annual herb), which have increased in volume with the implementation of ecological projects. Abandoned cropland (AC), which developed from CR and orchards in 2011(Liu et al., 2020), is mainly located at the bottom of the hillside. The area of natural vegetation (forest, shrubs, grass, AC) occupies about 83% of the Chenqi catchment area. The valley area in the center of the Chenqi catchment is well-developed, with cultivated CR covering 17% of the total catchment area (Yue et al., 2020), the rotation crops being rice, corn, rapeseed, and vegetables (e.g., tomato, cucumber, and beans). High-intensity fertilizer is usually applied to CR from May to July (for summer crops) and November (for winter crops). Chemical fertilizers and organic fertilizers are mainly used for summer crops (corn, vegetables, and paddy rice), while chemical fertilizers are mainly used for winter crops (rapeseed and spinach).

2.2. Soil sampling

Soil samples were collected from the four main types of land use in the Chenqi catchment, including CR, AC, shrubland and grassland (SG), and secondary forest (SF) (Fig. 1). Generally, the soil N content is mainly varied in the upper layer and constant in deep layer (Liu et al., 2020). Thus, an 80 cm-deep / 50 cm-diameter hole was excavated for soil profile sampling at each site. Samples were collected from the soil profiles with 10 cm intervals at the topsoil ranging from 0 to 30 cm (surface (0 – 5 cm), 10, 20, 30 cm) and 20 cm intervals below 30 cm depth (50 cm and 70 cm) in CR, AC, SG, and SF. Four sampling campaigns were conducted seasonally in April, July, September, and November 2017, which corresponded to major agricultural activities, such as sowing, growing, harvesting, and the fallow period after harvest, respectively.

2.3. Sample measurement

Samples for measuring soil moisture were collected at the corresponding depth (except the surface) by the cutting ring method; the 100 g wet soil samples were subjected to oven drying for 24 h, at 105 °C, and subsequently recorded the dry soil weight, to calculate the soil moisture (Susha Lekshmi et al., 2014). After removing coarse roots and stones, each soil sample was separated into two parts, air-dried for pH analysis, and further dried with a freezer dryer for analysis of N content and isotope values. Dry samples were passed through a 100-mesh sieve (<150 μm) for analysis of chemical properties. Soil pH (soil: water = 1:2.5) was measured using a portable pH meter, with a precision of ± 0.05. The dissolved N (NO_3^-、NH_4^+、TDN) was extracted with a 2 mol/L

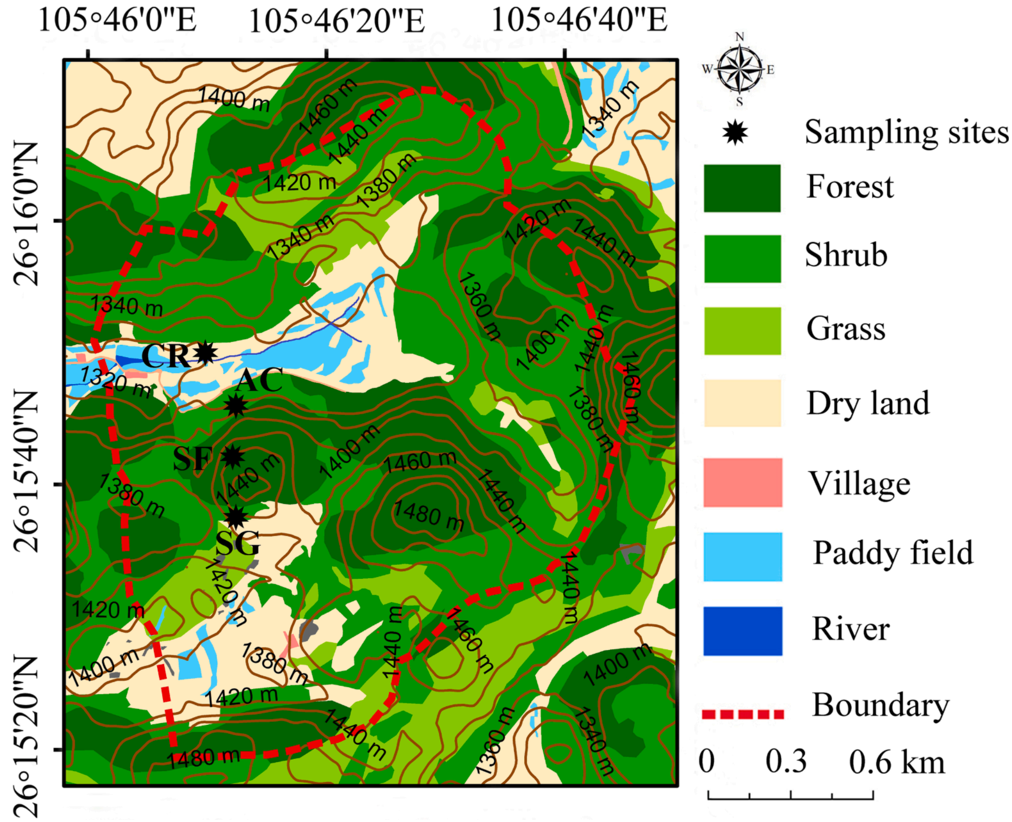

Fig. 1. Location nd land use of the Chenqi catchment.

KCl solution for 2 h in the shaker (Rock et al., 2011) and determined colorimetrically in a continuous flow analyzer (SKALAR Sans Plus Systems) after being filtered through 0.45 μm cellulose-acetate filters. The soil particulate organic N (PON) and carbon-to-nitrogen (C/N) ratio were determined with an automated elemental analyzer (Vario MAX CNS analyzer, Hanau, Germany) after dissolved N and carbon were removed by washing with a 2 mol/L KCl solution, a 0.1 mol/L HCl solution, and pure water (to wash samples to neutrality), and dried with a freezer dryer.

The stable N isotopic composition of PON (δ^{15}N-PON) was derived using the quartz tube melting sealing high-temperature combustion method (Oelmann et al., 2007; Hobbie and Ouimette, 2009). The PON was converted to N_2 and then analyzed with an isotope ratio mass spectrometer (Finigan MAT 252). Three international N standards: IAEA-N1 (0.4‰), IAEA-N2 (20.3‰), and IAEA-NO3 (4.7‰), were used for δ^{15}N-PON analysis calibration. The analytical precision for δ^{15}N-PON was better than 0.2‰. Dual isotopes (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) of dissolved nitrate (water extracted) were determined using the denitrifying bacteria method (McIlvin and Casciotti, 2011). Specifically, NO_3^- was converted to N_2O by denitrifying bacteria, purified by the trace gas pre-concentrator unit, and then analyzed with an isotope ratio mass spectrometer (IsoPrime, GV, UK). Four international standards: USGS-32, USGS-34, USGS-35, and IAEA-NO3, were used for δ^{15}N-NO_3^- and δ^{18}O-NO_3^- analysis calibration. The analytical precision of the dissolved nitrate isotope analysis method was 0.3‰ for δ^{15}N-NO_3^- and 0.5‰ for δ^{18}O-NO_3^-.

2.4. Data analysis and statistics

Isotope ratios are expressed as δ values and units defined as:

$$\delta(\%) = [(R_{sample}/R_{standard}) - 1] \times 1000 \quad (1)$$

where R_{sample} and $R_{standard}$ represent the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios of measured samples and the international standards, respectively.

The isotopic fractionation follows the Rayleigh distillation Equation (2):

$$\delta = \delta_0 + \varepsilon \ln(f) \quad (2)$$

where δ and δ_0 represent the residual isotope values and the initial isotope values, respectively, ε is the isotopic enrichment factor, and f is the remaining fraction (Kendall et al., 2007).

The differences in N content and isotope values between different land-use types of soil were analyzed using a combination of Multiple regression analysis and one-way analysis of variance.

3. Results

3.1. Soil moisture and pH

The soil pH of all samples ranged from 4.8 to 7.3 (Fig. S1), with a coefficient of variation (CV) of 5.8%. Most samples (94%) have pH values lower than 7.0; the lowest pH value was observed in CR, ranging from 4.8 to 6.9 (n = 24, CV = 7.0%). There was no significant difference ($P > 0.05$) in the soil pH of the four types of land use in soil profiles among the four sampling periods. The soil moisture content in soil profiles of four types of land use ranged from 20 to 45% (CV = 17.2%) (Fig. S2), and the highest and lowest soil moisture content was observed at SF and CR, respectively. There was a small seasonal variation of soil moisture in SF and SG relative to AC and CR. All soil profiles observed relatively low soil moisture content in April than in the other three times.

3.2. Soil nitrogen content

The PON content of all samples ranged from 0.8 to 8.6 g kg^{-1} (n = 93, CV = 57.8%) (Fig. 2). The PON content in all soil profiles decreased

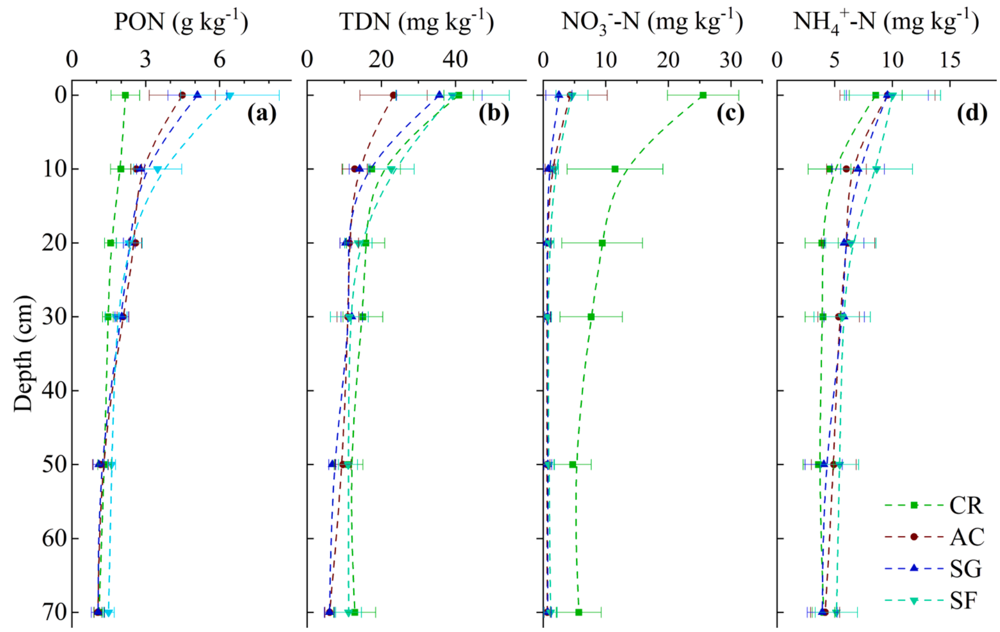

Fig. 2. The variation of (a) soil particulate organic nitrogen (PON), (b) total dissolved nitrogen (TDN), (c) NO_3^--N, and (d) NH_4^+-N content in soil profiles of four types of land use.

with depth from 0 to 30 cm, and remained constant at low values of 30 – 70 cm. The lowest average PON content (1.58 ± 0.49 g kg^{-1}) was observed in CR, and the highest PON content (8.6 g kg^{-1}) was detected at the surface of SF in April. The dissolved N (NO_3^-, NH_4^+, TDN) content showed a similar change trend in soil depths to that of PON of four types of land use (Fig. 2). The TDN, NH_4^+-N, and NO_3^--N content varied from 4.46 to 56.68 mg kg^{-1}, 2.13 to 13.80 mg kg^{-1} and 0.03 to 33.04 mg kg^{-1}, respectively. There was no significant difference ($P > 0.05$) in NH_4^+-N content in the soil profiles of the four types of land use, whereas NO_3^--N content presented a significant difference ($P < 0.05$). The soil samples of CR had higher NO_3^--N contents than other land-use soil samples, with an average value of 10.77 ± 8.87 mg kg^{-1}. The NO_3^--N content of non-agricultural land soil profiles (AC, SG, and SF) during four sampling periods was kept at low level, with an average value of 1.36 ± 2.09 mg kg^{-1}.

3.3. *Nitrogen isotope values and C/N ratio*

The δ^{15}N-PON values from CR, AC, SG, and SF were 5.5 – 7.6‰ (n = 93, CV = 8.0%), 3.1 – 7.4‰ (CV = 14.1%), 2.6 – 8.9‰ (CV = 23.6%) and 0.7 – 8.9‰ (CV = 32.8%), respectively (Fig. 3). The CV values from CR to SF displayed increased trend. The δ^{15}N-PON values increased with the soil depth of 0 – 30 cm and showed little variation in deep soil (>50 cm) in all soil profiles (Fig. 4). In surface soil, CR and SF had the highest and the lowest average δ^{15}N-PON values.

According to the high NO_3^--N content in CR and low content in other types of land use, the δ^{15}N-NO_3^- values of dissolved nitrate were only measured in CR soil profiles. δ^{15}N-NO_3^- values varied from −2.3 to 15.2‰ (CV = 58.8%), and the highest values were detected at 10 cm depth (Fig. 3). The C/N ratios of all samples varied from 5.2 to 17.0 (CV = 22.7%) (Fig. S3), the highest value was observed from CR, which ranged from 8.0 to 17.0 (CV = 18.1%). All soil profiles evidenced decreasing C/N ratios with increasing soil depths (Fig. S3).

4. Discussion

4.1. *Effects of land-use change on soil nitrogen content*

The organic N content could increase during land-use change when abandoned CR changes to grassland, shrubland, and forest (Aryal et al., 2018; Shen et al., 2020). In the present study, the PON content in CR, AC, SG, and SF increased following the evolution of land use after returning farmland to forests (Fig. 4), which is similar to other studies in the Southwest China karst area (Han et al., 2020; Liu et al., 2019). Among the four types of land use, CR is most affected by agricultural activities, such as fertilization input and crop harvesting, which corresponded to adding large amounts of N and removing organic N from CR, respectively. This may be the major reason for the dramatic changes in both PON and dissolved N in CR than other land uses.

The increases in PON input after agricultural abandonment promote the activity of soil microorganisms simultaneously (Li et al., 2018b; Coban et al., 2022). The study area's warm and humid subtropical monsoon climate is also conducive to N storage from organic matter to soil (Li et al., 2018a; Huang et al., 2020). Inorganic N produced from PON mineralization is the primary source for microbe uptake and plant growth in the natural ecosystem (Shan et al., 2019; Zhang et al., 2022). Dissolved N (TDN, NH_4^+, NO_3^-) content was kept at a low level and showed a similar vertical change with PON content in soil profiles of the natural ecosystem (AC, SG, and SF), indicating that PON mineralization regulated the dynamic of inorganic N in soil profiles. By comparison, although there was low PON content in CR, a large amount of chemical fertilizer was used and resulted in high TDN content (Fig. 4). Both PON and dissolved N content showed a similar variation at 0 – 30 cm (Fig. 2), suggesting that the effects of land use on N content mainly occurred at the top 30 cm soil layer. The cultivated layer in CR and the main area of soil microbes is usually in topsoil (Fierer et al., 2003; Li et al., 2018b; Sun et al., 2021), and PON input and microbial activities will be restricted in the soil layer where depths >30 cm (Han et al., 2020), which leads to low N content in the deep soil layer under all land-use soil profiles.

Large variation of PON and dissolved N (TDN, NH_4^+, NO_3^-) in topsoil and low variation in deep soil suggested that the land-use change after CR abandonment mainly affected topsoil N cycle, which vulnerable to lose N to karst aquatic environment during rainfall events (Wang et al., 2020; Yue et al., 2020). It should be noted that the decreased nitrate accumulation in topsoil following the land-use change indicated that CR abandonment can conduce to the N loss to aquatic system from karst catchment.

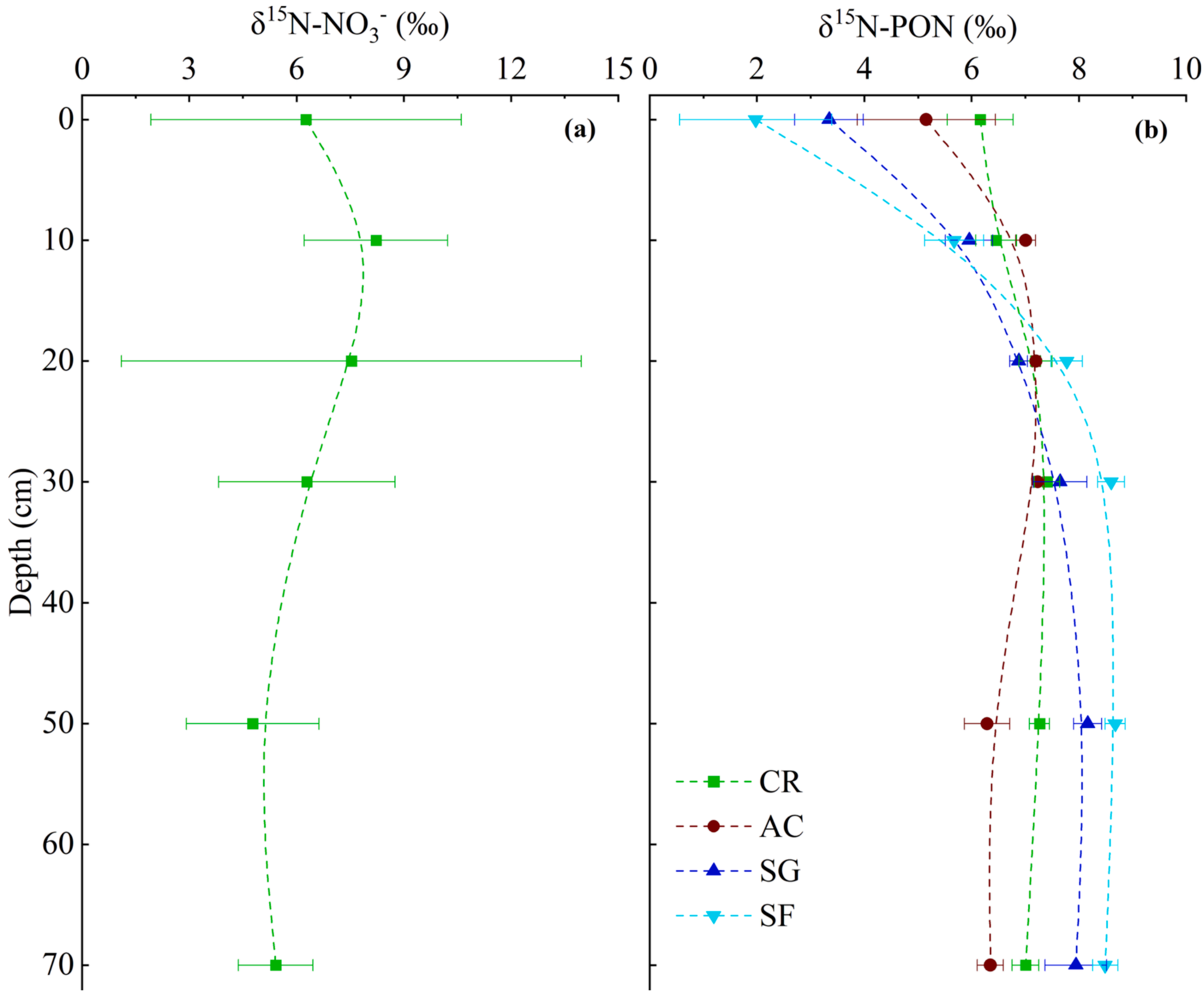

Fig. 3. The vertical variation of (a) dissolved nitrate nitrogen isotope values in cropland (CR) and (b) soil particulate organic nitrogen (PON) isotope values in soil profiles of four types of land use. The error bar mainly reflected the seasonal variation at same depths.

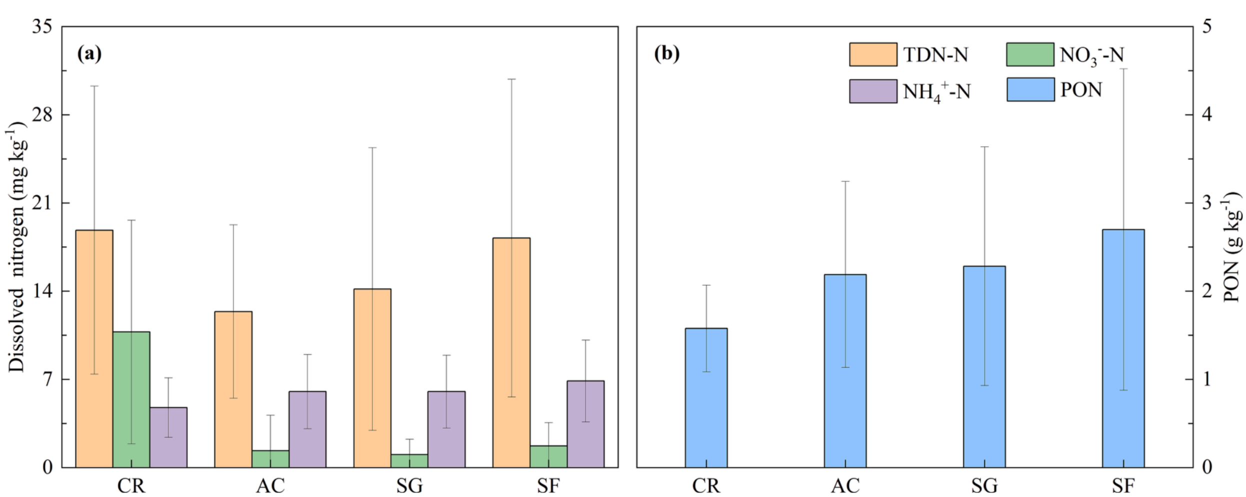

Fig. 4. (a) Dissolved nitrogen content and (b) particulate organic nitrogen in soils of four types of land use.

4.2. Changes in the transformation process after cropland abandonment

The characteristics of N content and isotopic signature can provide evidence for the analysis of N transformation in soil (Mikha et al., 2005; Manzoni et al., 2008). Decrease PON content and increased δ^{15}N-PON values in soil profiles indicated the occurrence of PON mineralization in Chenqi catchment, similar results were also reported by Han et al. (2020). Organic N is consumed continuously through mineralization under soil microbial activity and varied significantly in the soils of different types of land use (Kieloaho et al., 2016; Li et al., 2018a), which lead to active N acquisition after CR abandonment of the different degrees of N transformation in CR, AC, SG, and SF. Therefore, the different N content and δ^{15}N-PON values in soil samples after CR was abandoned also indicate that land-use change drove a change in the N cycle process in soil profiles.

Generally, topsoil received the degraded litter and presented higher N content and lower δ^{15}N-PON values, and both N input and microbial biomass decreased with soil depth (Basaran et al., 2008; Xu et al., 2022). The large variation of N content and isotope values in topsoil and nitrogen characteristics (stable and low N content, and high δ^{15}N-PON values) in deep soil revealed that N transformation mainly occurred in the topsoil layer. In CR, crop harvesting reduced PON input to soil, resulting in low PON content (1.58 ± 0.49 g kg^{-1}) and stable δ^{15}N-PON value (6.9 ± 0.5‰) in soil profiles of four types of land use.

The isotopic fractionation of mineralization was obtained from the slope of the relationship between δ^{15}N-PON and ln (PON) (Eq. (2), Fig. 5), which reflected the degrees of mineralization. According to the relationship between PON and δ^{15}N-PON in CR, AC, SG, and SF, the variation of isotopic fractionation caused by mineralization was different from the variation of PON content in four types of land use in Chenqi catchment. Soil moisture content, which corresponded to land use, was considered an important controlling factor for N transformation in the soil (Wang et al., 2006; Roberts et al., 2010). SF is mainly located on the upper slopes of the hillside and is relatively less affected by human activities, thereby having the high soil moisture and PON content of the soil in the four types of land use. A warm climate, large amounts of PON, and proper soil moisture promoted the occurrence of mineralization, which caused microbial activities more active with the highest δ^{15}N-PON fractionation (-5.0‰) in SF (Fig. 5). Due to the effect of the local agricultural activities, CR has the lowest PON and soil moisture content, and the lowest δ^{15}N-PON fractionation (-1.8‰) by mineralization. The PON and soil moisture content range in AC and SG were mediated between CR and SF, and the degree of δ^{15}N-PON fractionation was also higher than CR and lower than SF. Increasing the fractionation factor of δ^{15}N-PON from CR to AC and SF suggested that mineralization was enhanced after CR was abandoned.

Unlike organic N, inorganic N can be directly dissolved and utilized by plants (Jost et al., 2010). Mineralization consumed soil organic matter and produces NH_4^+-N, which is subsequently absorbed in the soil by the negatively charged soil colloid, providing an N source for plants and a substrate for nitrification to produce NO_3^--N (Kuypers et al., 2018). Nitrogen from nitrification and deposition is the primary nitrate source in non-agricultural land soil (Amundson et al., 2003; Buckeridge et al., 2009), whereas agricultural activities usually dominate the agricultural land soil N content (Li et al., 2022; Oelmann et al., 2007). In the Southwest China karst area, nitrate from deposition has a limited effect

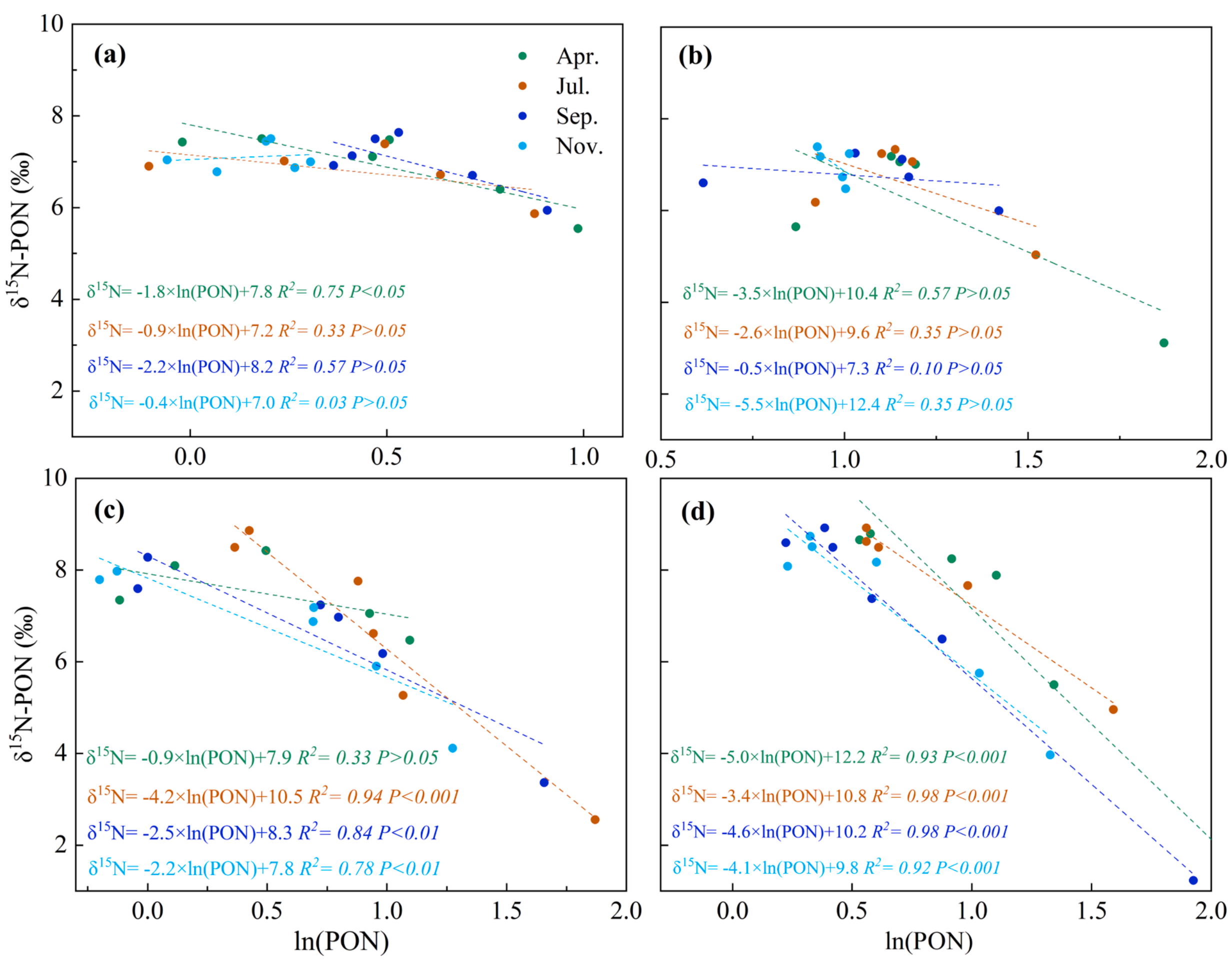

Fig. 5. The relationship between δ^{15}N-PON and Ln (PON) in the soil of four types of land use, a, b, c, and d represent cropland (CR), abandoned CR (AC), shrubland and grassland (SG), and secondary forest (SF), respectively.

on soil N content (Zeng et al., 2019), so NO_3^- in AC, SG, and SF should mainly originate from nitrification. Based on the $\delta^{15}N$-NO_3^- values, the main nitrate source in CR should be soil organic N (2 – 8 ‰), but if the low PON and high NO_3^--N content were considered, it can be inferred that inorganic N fertilizer or nitrification was the main nitrate source in CR soil.

Denitrification is a nitrate depletion process that usually occurs in an anaerobic environment (Kendall et al., 2007), and it was proved to be the critical reason for ^{15}N enrichment with soil depth (Hobbie and Ouimette, 2009). Previous studies found that denitrification rates were positively correlated with soil moisture content (Bai et al., 2017; Tan et al., 2018). In the present study, the high soil moisture content in deep soil would benefit denitrification. The occurrence of denitrification also further caused the lower NO_3^--N content in the deep soil than in topsoil in the Chenqi catchment. In summary, various N transformation processes affect the soil N content and isotope values, and the degree of the transformation varies from CR to AC, SG, and SF.

4.3. Implications for karst soil nitrogen loss control

Nitrogen loss across the soils of various land-use types can be qualitatively assessed by $\delta^{15}N$-PON values, N content, and the C/N ratio (Stevenson et al., 2010). Variations in $\delta^{15}N$-PON in four land-use soil profiles suggest that the extent of N loss may vary within these systems. The significant fluctuation of PON and dissolved N content and $\delta^{15}N$-PON values mainly occurred in the topsoil, indicating that N losses from the soil to surrounding waters (groundwater and surface water) primarily occurred in the topsoil in both CR and natural land uses (AC, SG, and SF).

The significant variation of C/N and $\delta^{15}N$-PON (Fig. 4) in the upper layer of four land-use types of soil indicates that karst forest topsoil may be the hotpot of the catchment organic N loss. The bioavailable organic N in soil provided the N required for microbial activities, e.g., mineralization, which in turn changed the N isotope value and C/N ratio in soil (Stevenson et al., 2010). The correlation between $\delta^{15}N$-PON and C/N ratio in four land uses soils (Fig. 6) suggested that organic N availability may be the primary factor in explaining the increases in $\delta^{15}N$-PON across all land uses. In natural land uses, more PON was converted to inorganic N in SF than in SG and AC, implying that SF might have more inorganic N loss from soil.

Unlike the N in AC, SG, and SF, N in CR was mainly dominated by land management practices, such as agricultural fertilization. Several studies have found that nitrate isotope values of Southwest China karst river water showed the signature of soil organic N source ($\delta^{15}N$-NO_3^- values ranging from 2 to 8‰), but derived from chemical fertilizers (Wang et al., 2022b; Yang et al., 2020a; Yue et al., 2020). According to the nitrate source assessment in this study, the average $\delta^{15}N$-NO_3^- value (6.3 ± 3.7‰) of dissolved nitrate of CR soil also implied they mainly originate from soil organic N. Nevertheless, high NO_3^--N and low PON content and slight variation of C/N and $\delta^{15}N$-PON in CR soil profiles suggested that chemical fertilizer, not PON, was the primary source of nitrate lost in CR. Overall, from the view of N content and isotope values in different depths of soil in CR, AC, SG, and SF, N loss control in karst catchment should mainly focus on the loss of fertilizer N from the topsoil of farmland.

5. Conclusion

This study aimed to assess the variation of N characteristics and the primary N transformation process in soil profiles after CR abandonment and to assess the N loss process from karst soil under a land-use change in a mixed land-use karst agricultural catchment in Southwest China. The main findings of the present study were as follows: both PON and dissolved N (NO_3^--N、NH_4^+-N、TDN) content decreased with soil depths, and a large variation was mainly contracted in 0 – 30 cm in the soil profiles of four types of land use, which suggests that the N transformation mainly occurred in the topsoil layer. Results showed that PON content increased after CR abandonment and revegetation. The NO_3^--N content of CR soil affected by agricultural activities is about 20 times that of non-agricultural soil (AC, SG, and SF). These results confirmed the hypothesis that N biogeochemical behaviors showed varied characteristics during the evolution of land use after CR abandonment. The opposite trend of $\delta^{15}N$-PON in a vertical direction with N content was detected in four land-use soils. Mineralization was the major transformation affecting PON content and $\delta^{15}N$-PON values, the highest ^{15}N fractionation caused by mineralization was detected in SF, with a

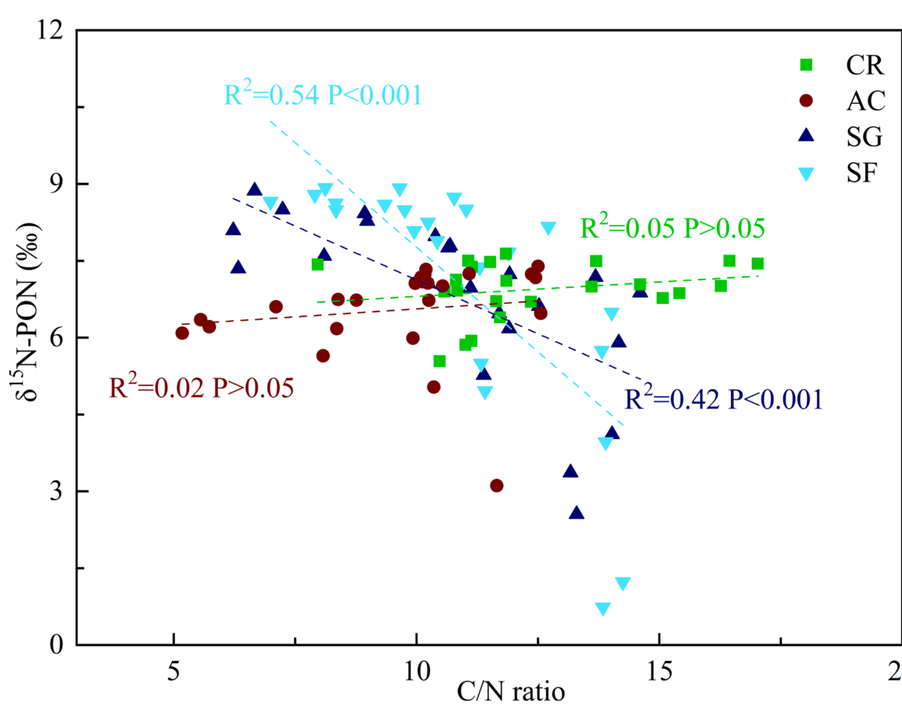

Fig. 6. The relationship between $\delta^{15}N$-PON and C/N ratio in soil samples of four types of land use.

fractionation factor of −5.0‰. The changes in N content and δ^{15}N-PON values from CR to SF indicated that N loss processes mainly occurred in the topsoil. The results highlighted CR abandonment could reduce N loss from soil, so the key to preventing N loss in karst area is to control the fertilizer N loss from the topsoil of CR, which implied that further catchment management should consider avoiding rough fertilization methods and spread scientific fertilization methods, e.g., slow-release fertilizer and organic nitrogen fertilizer application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This research was funded by the National Natural Science Foundation of China [grant numbers 42073076, 42230509, U1802241]; School-level research projects of Yancheng Institute of Technology [grant number xjr2021041].

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2023.107026.

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