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Natural vegetation restoration is more beneficial to soil surface organic and inorganic carbon sequestration than tree plantation on the Loess Plateau of China



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HIGHLIGHTS

- Effects of two ecological restoration measures on soil carbon were investigated.
- Natural grassland is more beneficial to SOC sequestration than tree plantation.
- Changes in content of SIC cannot indicate the SIC transformation and sink.
- DIC transportation from natural grassland could produce a potential carbon sink.
- Soil carbon isotopes can help in analyzing the inherent sequestration mechanism.

GRAPHICAL ABSTRACT



Difference in SOC/SIC accumulation and transportation

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ABSTRACT

Natural vegetation restoration and tree plantation are the two most important measures for ecosystem restoration on the Loess Plateau of China. However, few studies have compared the effects of the two contrasting measures on soil organic and inorganic carbon (SOC and SIC) sequestration or have further used SOC and SIC isotopes to analyze the inherent sequestration mechanism. This study examined a pair of neighboring small watersheds with similar topographical and geological backgrounds. Since 1954, natural vegetation restoration has been conducted in one of these watersheds, and tree plantation has been conducted in the other. The two watersheds have now formed completely different landscapes (naturally restored grassland and artificial forestland). Differences in soil bulk density, SOC and SIC content and storage, and SOC and SIC $\delta^{13}\text{C}$ values were investigated in the two ecosystems in the upper 1 m of the soil. We found that SOC storage was higher in the grassland than in the forestland, with a difference of 14.90 Mg ha^{-1} . The vertical changes in the $\delta^{13}\text{C}_{\text{SOC}}$ value demonstrated that the two ecosystems have different mechanisms of soil surface organic carbon accumulation. The SIC storage in the grassland was lower than that in the forestland, with a difference of 38.99 Mg ha^{-1} . The $\delta^{13}\text{C}_{\text{SIC}}$ values indicated that the grassland generates more secondary carbonate than the forestland and that SIC was most likely transported to the rivers from the grassland as dissolved inorganic carbon (DIC). The biogeochemical characteristics of the grassland were favorable for the formation of bicarbonate. Thus, more DIC derived from the dissolution of root

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and microbial respired CO₂ into soil water could have been transported to the rivers through flood runoff. It is necessary to study further the transportation of DIC from the grassland because this process can produce a large potential carbon sink.

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1. Introduction

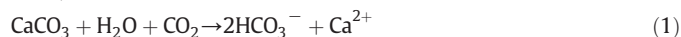
Anthropogenic CO₂ emissions into the atmosphere represent the largest human contribution to climate change in the past 100 years (Canadell et al., 2007). Accumulating carbon in the terrestrial biosphere is considered a promising option for mitigating the buildup of atmospheric CO₂ (Schlesinger, 1999; Scholes and Noble, 2001; Lal, 2004a). Soil is the largest carbon pool in terrestrial ecosystems, storing approximately 1550 Pg (1 Pg = 10¹⁵ g) of soil organic carbon (SOC) and 950 Pg soil inorganic carbon (SIC) (Batjes, 1996), more than three times the quantity of carbon in the biota or the atmosphere (Lal, 2004a). Previous studies have shown that the carbon sequestration potential of global soils is 0.4–1.2 Pg C yr⁻¹, or 5–15% of global fossil fuel emissions (Lal, 2004a). However, there is uncertainty about the size and global distribution of the pools and fluxes of carbon in the soil (Houghton, 2003). To assess the carbon sequestration potential of terrestrial ecosystems for mitigating global climate change, it is important to have a comprehensive understanding of the magnitudes of the carbon sink and accumulation mechanisms operating under different vegetation and ecosystem management strategies (Schimel et al., 2001; Ciais et al., 2008; Huang et al., 2010; Pan et al., 2011).

Natural vegetation restoration and tree plantation are two important measures for the remediation of degraded ecosystems. Many previous studies have demonstrated that both measures can significantly promote soil carbon storage (Houghton et al., 1999; Lal, 2004b; Woodbury et al., 2007; Piao et al., 2009; Huang et al., 2012). Compared with tree plantation, natural vegetation restoration requires a long-term process to restore the function of the ecosystem. Therefore, many countries, especially developing countries, have chosen tree plantation as a priority method of promoting ecosystem restoration and carbon sequestration (Watson et al., 2000). In China, for example, 28 million ha of plantations was established from 2000 to 2005 (Chazdon, 2008), and a commitment has been made to increase forest area by 40 million ha from 2006 to 2020 to reduce the associated carbon footprint (Yin et al., 2010; Cao et al., 2011). In humid regions, it is appropriate to use tree plantation to promote ecosystem restoration and carbon sequestration, although this method has raised grave concerns in arid and semiarid regions (Cao et al., 2010; Wang and Cao, 2011). Currently, there is a great need to compare the effects of natural vegetation restoration and tree plantation on soil carbon storage and distribution. The resulting information will help in assessing the carbon benefits resulting from various restoration measures.

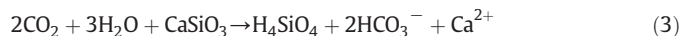
SOC is the focus of most studies in terrestrial carbon research because of its importance in regulating ecosystem function and the greenhouse effect (Lal, 2004a). However, the soil carbon pool includes two principal components, SOC and SIC (Schlesinger, 1982; Batjes, 1996). Because SIC is the most common form of carbon in arid and semiarid regions, the SIC pool and its dynamics are much more important than previously recognized (Schlesinger, 1999; Lal and Kimble, 2000; Emmerich, 2003; Mi et al., 2008; Wang et al., 2010). For example, Xie et al. (2009) have found that inorganic carbon absorption by saline/alkaline soils in northwest China could be as high as 62–622 g C m⁻² yr⁻¹, orders of magnitude greater than the previously reported carbonate accumulation rates of desert ecosystems (Schlesinger, 1982, 1985; Lapensis et al., 2008). Although this result has been questioned (Stone, 2008; Schlesinger et al., 2009), this uncertainty also indicates that a better understanding is needed for SIC dynamics and processes in arid and semiarid regions.

The SIC pool comprises two components: lithogenic inorganic carbon (LIC) and pedogenic inorganic carbon (PIC). The former is inherited

from the parent material of the soil; the latter is formed through the dissolution and precipitation of carbonate parent material and consumes a mole of atmospheric CO₂ during carbonate dissolution, but it liberates an equal amount during pedogenic carbonate precipitation (Wu et al., 2009):



Eqs. (1) and (2) indicate that pedogenic carbonate formation cannot produce a net increase in SIC. However, if the DIC formed through the dissolution of root- and microbial-derived CO₂ into soil water (CO₂-H₂O) and carbonate (CaCO₃-CO₂-H₂O) was transported to rivers primarily through surface and subsurface runoff, this type of carbon transportation could produce a large potential carbon sink (Liu et al., 2010). Moreover, the process of calcrete reservoir weathering can also lead to the sequestration of atmospheric CO₂ on land. This process consumes two moles of atmospheric CO₂ for every mole released during the precipitation of pedogenic carbonate (Wu et al., 2009):



In recent years, an increasing number of studies have found that soil δ¹³C analysis is helpful in interpreting the mechanisms of SOC accumulation (Leavitt et al., 1994; Bird and Pousai, 1997; Ehleringer et al., 2000; Wynn et al., 2006; Wei et al., 2012). Surface soil generally has a much lower δ¹³C value due to the influence of a high input of new carbon and the Suess effect (the decline of ¹³C atmospheric CO₂ values with the burning of fossil fuels since the Industrial Revolution) (Friedli et al., 1986; Yu et al., 2005; Alewell et al., 2011). With increasing depth, plant carbon input decreases and the content of ¹³C-enriched stable carbon increases, producing a sensitive indicator of changes in the value of δ¹³C (Ehleringer et al., 2000). Wei et al. (2012) have indicated that soil δ¹³C is a more sensitive index than SOC content for analyzing the dynamics of SOC, which are comprehensively controlled by soil carbon input and decomposition. In addition to soil organic δ¹³C, soil inorganic δ¹³C can be used to analyze the weathering and precipitation process of carbonate (Karim and Veizer, 2000; Das et al., 2005; Li et al., 2008; Renforth et al., 2009). The above analysis shows that the SIC pool is composed of LIC and PIC and that the two different pools have different δ¹³C values. The LIC pool is inherited from parent material and generally presents high δ¹³C values, whereas the PIC pool results from the precipitation of carbonate ions derived from root and microbial respiration and calcium ions yielded by weathering reactions and generally presents low δ¹³C values (Cerling et al., 1989; Boutton, 1991; Rao et al., 2006; Li et al., 2013). Therefore, the soil inorganic δ¹³C value can be of substantial assistance in analyzing the inherent mechanism of SIC sequestration and transformation.

The Loess Plateau of China is a unique geographical unit characterized by extensive loess distribution, serious soil erosion, low vegetation coverage, and high soil carbonate content. Since the 1950s, the Chinese government has made great efforts to control soil erosion and restore vegetation, including large-scale tree plantation in the 1970s, integrated soil erosion control in the 1980s and 1990s, and the “Grain for Green

Project” in the 2000s (Chen et al., 2007; Zhou et al., 2013; Zhao et al., 2013). Currently, the ecological restoration of the Loess Plateau has produced remarkable achievements: an increase in vegetation coverage, a decrease in soil erosion, and an enhancement of ecosystem services (Lü et al., 2012; Feng et al., 2013). Soil carbon sequestration is a critical index for evaluating the efficiency of ecological restoration. Previous studies have unanimously indicated that ecological restoration significantly promotes soil carbon storage (e.g., Chen et al., 2007; Wei et al., 2009; Chang et al., 2011; Wang et al., 2011; Feng et al., 2013; Qiu et al., 2013; Zhan et al., 2013). However, most of these studies have focused on SOC, with only a few investigating SIC (Zhang, 2012; Chang et al., 2012; Tu et al., 2012). The results of these studies show that the mean density and storage of SIC in the 0–100 cm soil layer on the Loess Plateau are more than twice that of the SOC pool (Liu et al., 2011; Zhang, 2012) and represent 21.66% of the total SIC storage in China (Mi et al., 2008). Therefore, the SIC pool of the Loess Plateau may make an important contribution to the national carbon budget. Moreover, natural vegetation restoration and tree plantation are the two most important measures for ecosystem restoration. However, few studies have compared the effects of the two contrasting measures on SOC and SIC sequestration or have further used soil organic and inorganic carbon isotopes to analyze the inherent sequestration mechanism. This study examined two neighboring small watersheds on the Loess Plateau with similar topographical and geological backgrounds. Since 1954, natural vegetation restoration has been conducted in one of

these watersheds and tree plantation in the other. The watersheds have now formed completely different vegetation landscapes (DZG: grassland; YJG: forestland). The objectives of this study were to (1) examine the difference in SOC and SIC sequestration between natural vegetation restoration and tree plantation and (2) identify the inherent mechanism of carbon cycling using the soil organic and inorganic carbon isotope method.

2. Materials and methods

2.1. Study site

This study was conducted in the Nanxiaohe Basin, located in the Xifeng District of Qingyang city, Gansu province (Fig. 1). The region has a semi-arid continental climate with a mean annual temperature of 9.3 °C and an average annual precipitation of 556.5 mm. The precipitation from June to September represents 67.3% of the annual precipitation. The area has a hilly loess landscape with elevations varying from 1050 m to 1423 m. The soil layer is approximately 250 m thick, and the soil type is silt loam (Li, 2006).

In the basin, a pair of small neighboring watersheds with similar topographical and geological backgrounds, Dongzhuanggou (DZG) and Yangjiagou (YJG), was selected to compare the effects of natural vegetation restoration and tree plantation on soil carbon storage and distribution. DZG is 1.6 km long and has an area of 1.15 km². Since 1954, DZG

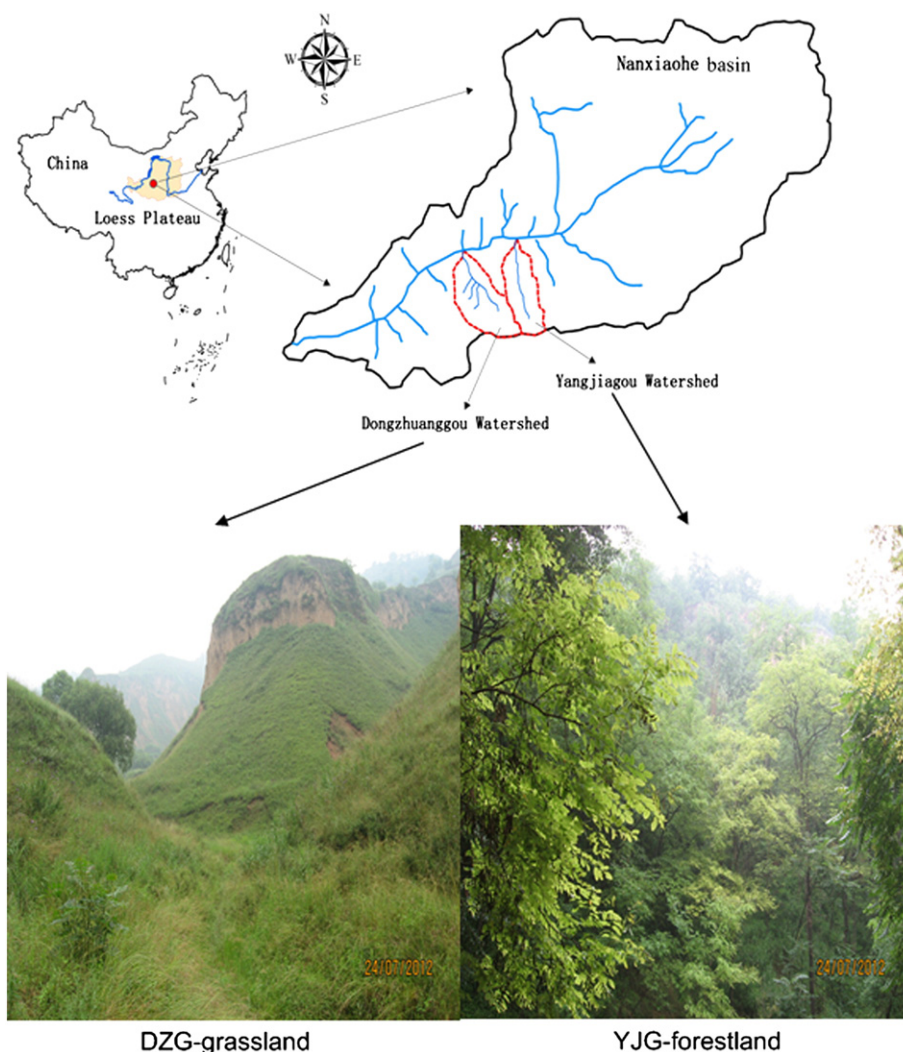


Fig. 1. Map showing the location of the study area in Xifeng District, Qingyang City, Gansu Province, including the Dongzhuanggou (DZG) watershed and the Yangjiagou (YJG) watershed.

has been subject to natural vegetation restoration measures, and it now supports grassland vegetation. The principal grass species are *Arundinella hirta*, *Agropyron cristatum*, and *Artemisia argyi*. YJG is 1.5 km long and has an area of 0.87 km². The principal afforestation activities in the YJG occurred in 1954–1958, and the current timber volume is 4000 m³ (Li, 2006). The principal planted species are *Robinia pseudoacacia*, *Platycladus orientalis*, *Pinus tabuliformis*, *Prunus sibirica*, *Populus davidiana*, and *Salix matsudana*. After 60 yr of vegetation restoration and construction, the two small watersheds have formed completely different vegetation landscapes (DZG: grassland; YJG: forestland). The original purpose of the two small watersheds was to compare the effects of ecological management and non-management on soil erosion. However, the contrasts also provide an opportunity to examine the difference in soil organic and inorganic carbon sequestration.

2.2. Soil sampling and laboratory analysis

Soil sampling was performed in May and September, 2013. To obtain the average content and vertical distribution of SOC and SIC, 14 sampling sites were established in the DZG-grassland and 14 in the YJG-forestland. The sampling sites were randomly distributed on the gully slopes, and soil samples were collected to a depth of 1 m. Soils were sampled at intervals of 10 cm using a hand-held auger (6 cm in diameter), and 10 soil samples were obtained at each site. Accordingly, 140 soil samples were obtained in the grassland and 140 in the forestland. Three soil profiles at a depth of 0–100 cm were established in the grassland and three in the forestland to measure the soil bulk density (BD) and $\delta^{13}\text{C}$ values. Three replicate samples at intervals of 10 cm were taken for soil BD analysis using a soil corer (a stainless steel cylinder 100 cm³ in volume) for each profile. Soil samples at the same distance intervals were collected and used to analyze soil organic and inorganic $\delta^{13}\text{C}$.

All the collected soil samples were air dried in the laboratory, and gravel and roots in the soil were carefully removed. The air-dried soil samples were ground in an agate mortar and passed through a 0.15 mm sieve. For the determination of SOC content, the soil samples were digested in K₂Cr₂O₇–H₂SO₄ solution using a heated oil bath, and the organic carbon concentration was then determined by titration (Bao, 1999). The SIC content was analyzed using the CM140 Total Inorganic Carbon Analyzer (UIC, Inc. Rockdale, Illinois, USA), which combines a self-contained unit for the acidification of a sample (to evolve CO₂) with a highly sensitive CO₂ detector and allows the direct measurement of total inorganic carbon in a wide variety of sample matrices and concentrations. The soil samples for BD were dried at 115 °C for 24 h. The SOC and SIC storage (Mg ha⁻¹) values were calculated as follows:

$$\text{SOC} = \sum_{i=1}^n D_i \times \text{BD}_i \times \text{OC}_i / 10 \quad (5)$$

$$\text{SIC} = \sum_{i=1}^n D_i \times \text{BD}_i \times \text{IC}_i / 10 \quad (6)$$

where D_i , BD_i , OC_i , and IC_i represent the soil thickness (cm), bulk density (g cm⁻³), organic carbon content (g kg⁻¹), and inorganic carbon content (g kg⁻¹), respectively, of the i th horizon of the soil profile.

For the determination of the SOC isotope composition, approximately 5 g of sieved soil sample was steeped in 2 M HCl for 24 h to remove the inorganic carbon. The samples were then washed with distilled water until the pH exceeded 5 and were dried at 40 °C. The dried samples were combusted for 2 h at 850 °C in an evacuated sealed quartz tube in the presence of silver foil and cupric oxide (Wei et al., 2012). For the determination of the SIC isotope composition, the sieved soil sample was allowed to react with 100% H₃PO₄ for 2 h at 75 °C to

generate CO₂ (Ning et al., 2006). Carbon isotope ratios ($\delta^{13}\text{C}$) were determined using an MAT-252 gas source mass spectrometer with a dual inlet system. The CO₂ gas was extracted and purified cryogenically, and the isotope composition of the extracted CO₂ gas was analyzed with the spectrometer. The ¹³C/¹²C ratio was expressed in δ notation as parts per thousand deviations (‰) from the Pee Dee Belemnite (PDB) standard:

$$\delta^{13}\text{C} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \right] \times 1000 \quad (7)$$

where R is the ¹³C/¹²C ratio. The analytical precision with the running standard (MAT-252) was 0.2% (Wei et al., 2012).

2.3. Statistical analyses

An independent-samples t -test was performed to test the significance of the differences in soil BD, SOC and SIC content, and storage at an alpha level of 0.05 ($\alpha = 0.05$) between the DZG-grassland and YJG-forestland. All statistical analyses were performed with the Statistical Program for Social Sciences (SPSS 11.0, SPSS Inc., 2001). The figures were processed in Excel 2003 and Grapher 8.

3. Results

3.1. Soil bulk density

The soil BD differed between the DZG-grassland and YJG-forestland (Fig. 2). The soil BD in the forestland increased gradually from 1.29 g cm⁻³ in the top layer to 1.51 g cm⁻³ in the deepest layer, whereas the soil BD in the grassland fluctuated. In the entire soil profile, the soil BD of the forestland (mean BD = 1.45 g cm⁻³) was greater than that of the grassland (mean BD = 1.34 g cm⁻³).

3.2. SOC content and storage

The SOC content showed substantial differences between the DZG-grassland and the YJG-forestland (Fig. 3). In contrast to the soil BD, the SOC content of the forestland was lower than the SOC of the grassland, averaging 5.22 and 3.84 g kg⁻¹, respectively. The vertical changes in SOC content showed that most of the SOC accumulated in the surface soils and that the SOC content decreased significantly in the 0–30 cm soil layers. The grassland stored more SOC than the forestland. The

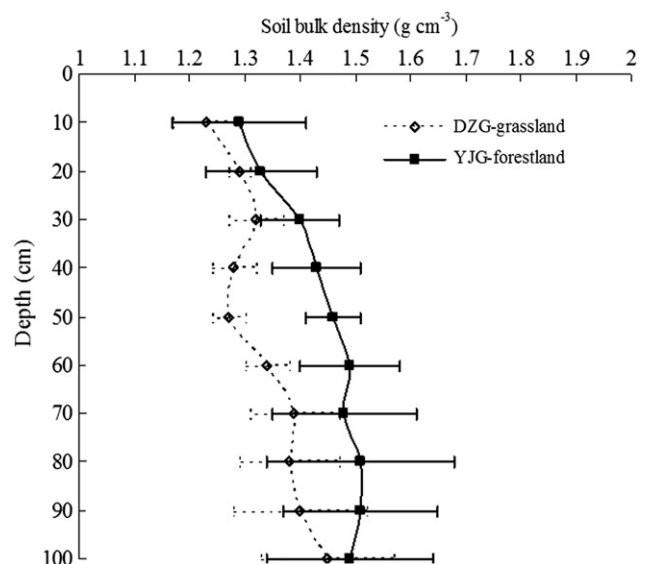


Fig. 2. Differences in soil bulk density between the DZG-grassland and the YJG-forestland.

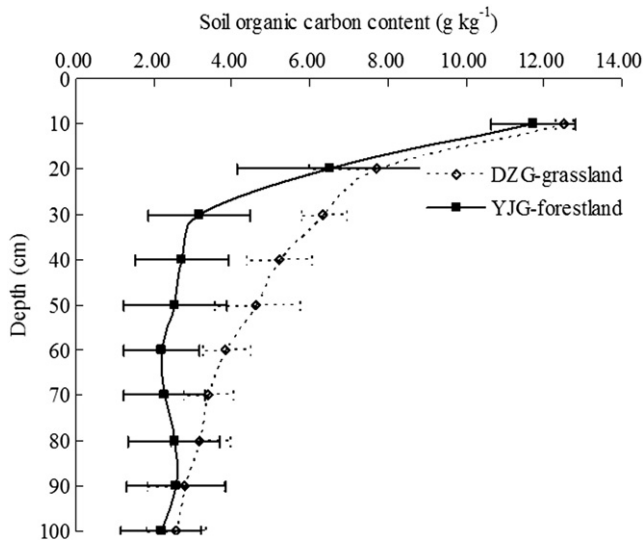


Fig. 3. Differences in SOC content between the DZG-grassland and the YJG-forestland.

amounts of SOC to a depth of 1 m in the forestland and in the grassland were 52.94 and 67.84 Mg ha⁻¹, respectively (Fig. 4a). In the 0–100 cm soil layer, the SOC stored in the top 30 cm represented 53.54% and 49.59% of the totals for the forestland and grassland, respectively (Fig. 4b).

3.3. SIC content and storage

The SIC content also differed between the DZG-grassland and the YJG-forestland (Fig. 5). The forestland showed a higher SIC content than the grassland. The mean values were 15.97 and 14.55 g kg⁻¹ for YJG and DZG, respectively. The SIC content in the forestland gradually increased with depth, whereas the SIC content of the grassland fluctuated in the deep soil layers. The forestland stored more SIC than the grassland. The amounts of SIC in the first 1 m of soil in the forestland and in the grassland were 233.28 and 194.29 Mg ha⁻¹, respectively (Fig. 6a). The proportion of SIC storage changed little among soil layers (Fig. 6b).

3.4. δ¹³C values of SOC and SIC

The δ¹³C values of SOC and SIC differed between the DZG-grassland and YJG-forestland (Fig. 7). The grassland showed higher δ¹³C_{SOC} values than the forestland. These values ranged from -22.09‰ to -20.32‰ and from 23.08‰ to -21.48‰, respectively. The vertical changes in δ¹³C_{SOC} showed that the grassland displayed a marked increase in soil δ¹³C values in the top 20 cm; in the forestland, however, the δ¹³C_{SOC} values varied relatively little. The δ¹³C values of SIC showed that the grassland had lower values of δ¹³C_{SIC} than the forestland, with values ranging from -5.87‰ to -6.19‰ and from 5.11‰ to 5.48‰, respectively. The grassland showed an evident decrease of δ¹³C_{SIC} values with depth, whereas the forestland showed a slight increasing trend (Fig. 8).

4. Discussion

4.1. The effects of natural vegetation restoration and tree plantation on SOC sequestration and the implications of δ¹³C_{SOC} for the mechanism of SOC accumulation

In the areas investigated by this study, natural vegetation restoration and tree plantation have formed completely different landscapes in the DZG and YJG after 60 years of vegetation restoration and construction. Currently, the DZG watershed is a forestland ecosystem, whereas the YJG watershed is a grassland ecosystem. The patterns of the soil carbon

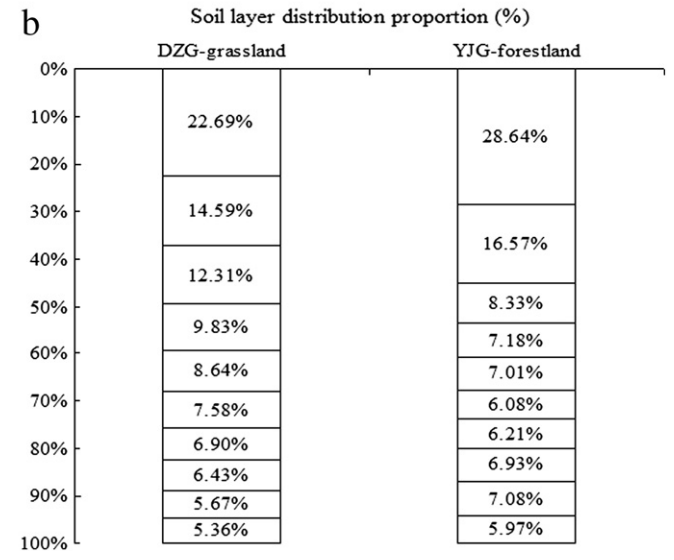
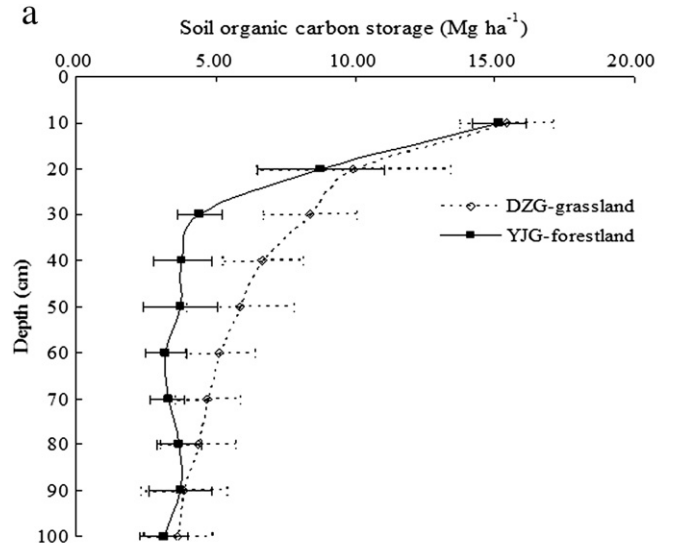


Fig. 4. Storage of SOC (a) and various soil layer distribution proportions (b) in the DZG-grassland and the YJG-forestland.

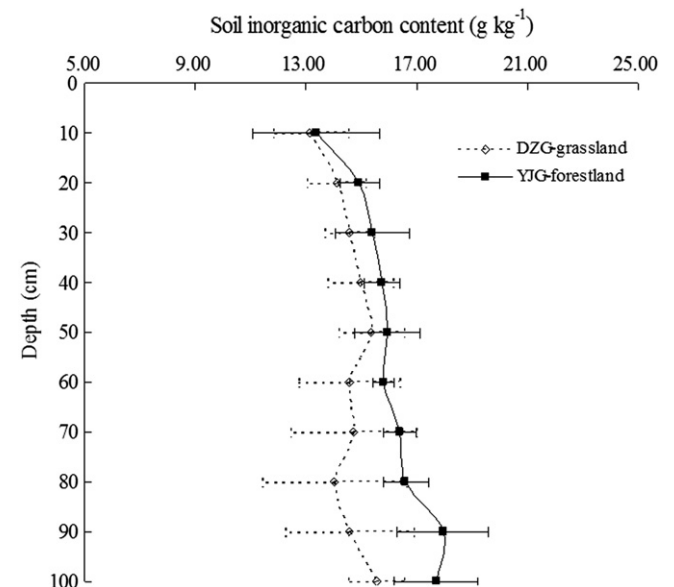


Fig. 5. Differences in SIC content between the DZG-grassland and the YJG-forestland.

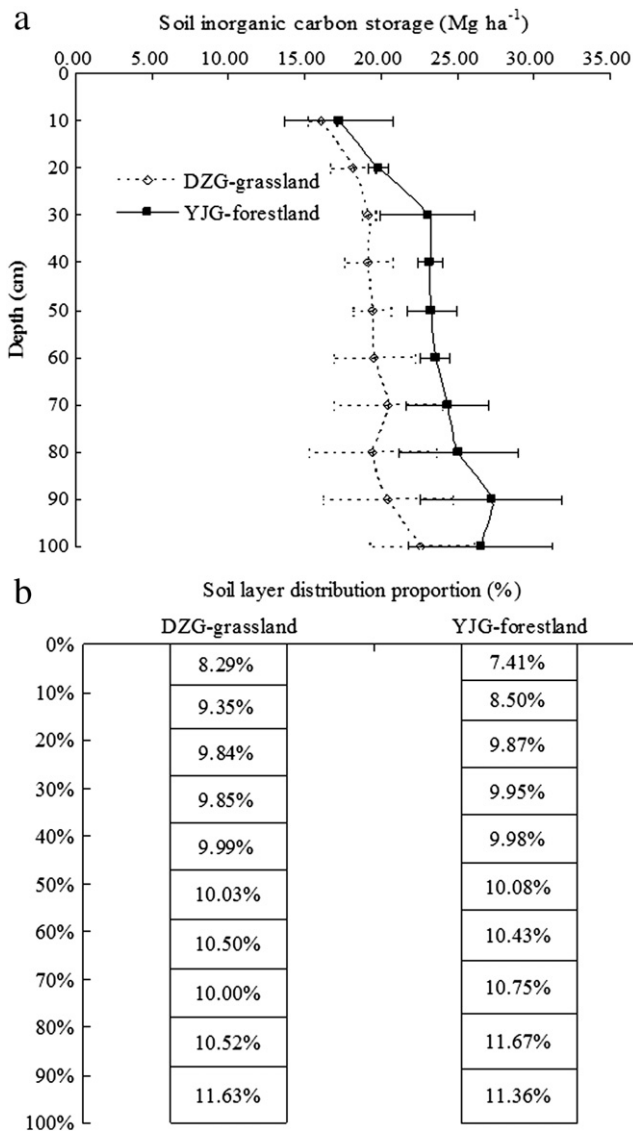


Fig. 6. Storage of SIC (a) and various soil layer distribution proportions (b) in the DZG-grassland and the YJG-forestland.

cycle in the two ecosystems clearly differ, but the magnitude of the difference is poorly understood. Our results showed that the DZG-grassland stored 14.90 Mg ha^{-1} more SOC than the YJG-forestland (Fig. 4a). This result indicates that naturally restored grassland is more beneficial to surface SOC sequestration than tree plantation. This finding is in agreement with the results of many previous studies. For example, Lugo and Brown (1993) found that tropical grasslands could accumulate more SOC than the adjacent forests; Tate et al. (2000) reported that the SOC storage in the total profile was 13% higher in a grassland than in a forest; a review by Conant et al. (2001) reported that conversion from native land cover (primarily rain forests) to grassland increased the soil carbon content in nearly 70% of the reviewed studies; Guo and Gifford (2002) indicated that soil carbon stocks could be higher under natural grassland than under natural forest. On the Loess Plateau, many studies have found similar results. In native grassland and adjacent woody lands of the northern Loess Plateau, Wei et al. (2009) found that the native grassland was more effective in soil surface organic carbon accumulation. Moreover, Wang et al. (2011) found that the ecological succession of grassland communities had a significant effect on SOC sequestration, whereas no such effect was detected for forests in the central Loess Plateau. Through a comparative study of the

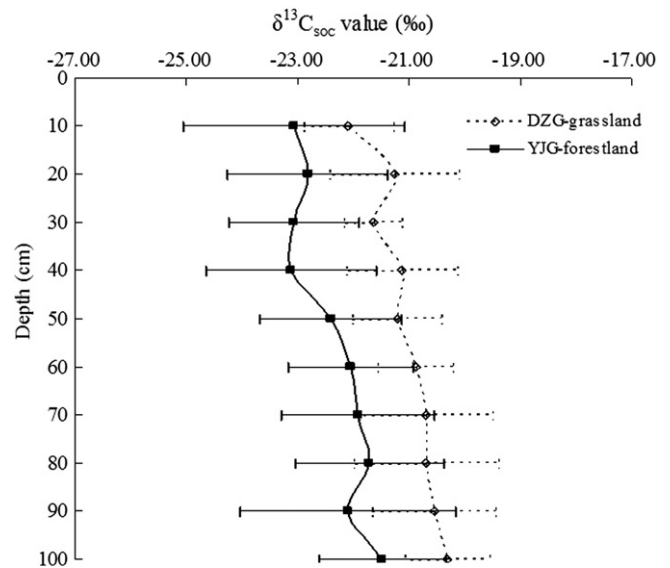


Fig. 7. Changes in soil $\delta^{13}\text{C}_{\text{SOC}}$ values with depth in the DZG-grassland and the YJG-forestland.

western Loess Plateau, Wei et al. (2012) found that naturally restored grassland would be a more effective vegetation type for SOC sequestration due to a higher carbon input from roots.

A large number of studies have demonstrated that the measurement of $\delta^{13}\text{C}_{\text{SOC}}$ values with depth could provide more detailed information than SOC content in analyzing the mechanisms of SOC accumulation. For a soil profile, the variation in soil $\delta^{13}\text{C}$ values with depth is primarily influenced by SOC decomposition, the mixing of new carbon with old, and the Suess effect (Friedli et al., 1986; Nadelhoffer and Fry, 1988; Ehleringer et al., 2000; Alewell et al., 2011). Wei et al. (2012) reported that the Suess effect was minimal on the Loess Plateau and that SOC decomposition and the mixing of new carbon with old were the principal factors controlling the vertical changes in the $\delta^{13}\text{C}_{\text{SOC}}$ value. In general, plant litter has a relatively low $\delta^{13}\text{C}$ value. Thus, the input of plant carbon can produce lower $\delta^{13}\text{C}_{\text{SOC}}$ values (Troluer et al., 1996; Yu et al., 2005). At the soil surface, most of the carbon is derived from the above-ground litter and, therefore, shows the most negative values of $\delta^{13}\text{C}_{\text{SOC}}$; with increasing depth, the plant carbon input decreases, and the

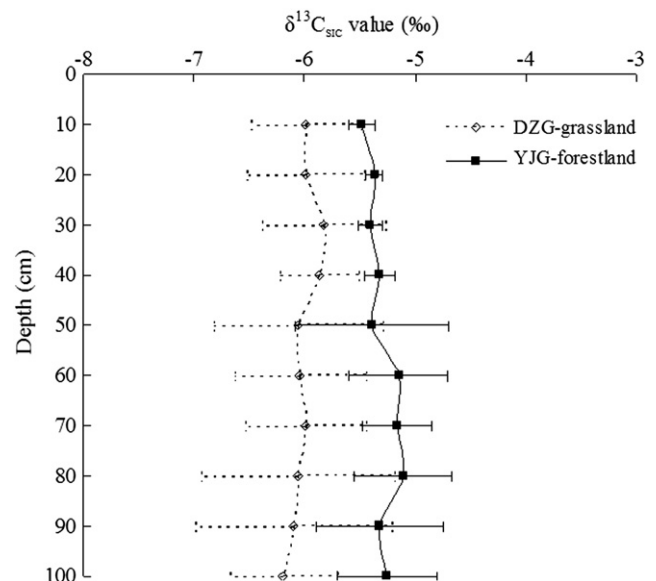


Fig. 8. Differences in soil $\delta^{13}\text{C}_{\text{SIC}}$ values between the DZG-grassland and the YJG-forestland.

proportion of ^{13}C -enriched microbial-derived carbon increases, producing an increase in $\delta^{13}\text{C}_{\text{SOC}}$ values (Ehleringer et al., 2000). In this study, the SOC content in the forestland decreased markedly in the top 30 cm and then varied little in the deeper soil layers, indicating that the principal carbon input was derived from the top soil layer. However, the $\delta^{13}\text{C}_{\text{SOC}}$ values of the forestland showed relatively small variation from the soil surface to a depth of 40 cm (Fig. 7), indicating that the stored carbon in the top soil layer was not derived primarily from the aboveground litter but, most likely, from the fine roots of the understory plants, which were primarily distributed in the surface layer of the soil. Similar to the forestland, the grassland displayed a marked decrease in SOC content in the surface soils (0–20 cm). However, in contrast to the deep soils of the forestland, the deep soils of the grassland still maintained a relatively high carbon content (Fig. 3), indicating that the fine grass roots densely distributed in the deep soil layers could play an important role in subsurface SOC accumulation. Moreover, the grassland displayed a marked increase in $\delta^{13}\text{C}_{\text{SOC}}$ values in the top soil layers (0–20 cm) (Fig. 7), showing that the principal input of surface soil carbon in the grassland is most likely derived from the aboveground litter.

4.2. The effects of natural vegetation restoration and tree plantation on SIC sequestration and the implications of $\delta^{13}\text{C}_{\text{SIC}}$ for the mechanism of SIC transformation

SIC represents the largest soil carbon pool on the Loess Plateau. The amount of SIC to a depth of 1 m is 10.20 Pg C, more than twice the corresponding SOC pool (Liu et al., 2011; Zhang, 2012). However, the factors affecting the dynamics of SIC are poorly understood. Recently, Chang et al. (2012) examined the effects of land use conversion from cropland to forest on SIC content in the central Loess Plateau and concluded that this type of land use change could redistribute SIC along the soil profile but would not affect the net SIC accumulation. Moreover, Zhang (2012) investigated the effects of different vegetation types on SIC content and found that the density of SIC in forestland and shrubland is higher than that in grassland and cropland. In this study, we also found that forestland showed a higher content of SIC than grassland, a difference of 0.39 kg m^{-2} . However, it is difficult to conclude that forestland has a greater potential as a SIC sink than grassland due to the changes in SIC content because the SIC pool is composed of LIC and PIC. Geochemical studies of loess have shown that the LIC and PIC of the Loess Plateau have different $\delta^{13}\text{C}$ values (Wen, 1989; Gu, 1991; Ning et al., 2006). The LIC is transported from a region where dust originates, and it shows high $\delta^{13}\text{C}$ values (Wang et al., 2005; Cao et al., 2008), whereas the PIC results from the dissolution and precipitation of carbonate parent material and presents low $\delta^{13}\text{C}$ values (Wen, 1989). Therefore, the difference between the $\delta^{13}\text{C}$ values of LIC and of PIC can be used to analyze the dynamics of SIC.

In this study, we found that the grassland showed lower values of $\delta^{13}\text{C}_{\text{SIC}}$ than the forestland. The average values were -6.01% and -5.30% , respectively, indicating that the grassland generates more secondary carbonate than the forestland. It is clear that the dissolution and precipitation of carbonate cannot result in net SIC accumulation, as a mole of atmospheric CO_2 is consumed during carbonate dissolution, but an equal amount is liberated during pedogenic carbonate precipitation (Lal and Kimble, 2000; Emmerich, 2003; Wu et al., 2009; Zhang, 2012). Therefore, the two ecosystems should, theoretically, show the same SIC content even if more LIC has been transformed into PIC. However, we found that the forestland had a higher SIC content than grassland, a result that contradicted the theoretical prediction. We speculate that the missing SIC of the grassland is most likely transported to the rivers through flood flow. Previous studies have shown that the soil water regime of the grassland is superior to that of the forestland (Huang et al., 1999; Wang et al., 2004). The good soil water condition, dense fine grass roots and abundant soil organic matter favor the formation of bicarbonate and thus accelerate the dissolution of carbonate in

the grassland, especially during rainy periods. DIC moves readily via surface and subsurface runoff. The vertical changes in $\delta^{13}\text{C}_{\text{SIC}}$ illustrated that the grassland displayed an obvious decrease in $\delta^{13}\text{C}_{\text{SIC}}$ values with depth, whereas the forestland displayed a slightly increasing trend (Fig. 8), indicating that the grassland is effective in DIC leaching. Moreover, the annual flood runoff and sediment discharge of the grassland were observed to be greater than that of the forestland (Fig. 9). Thus, more DIC could have been transported to the rivers and, subsequently, to the reservoir or ocean sediments to produce a long-term carbon sink. Liu et al. (2010) reported that this new type of carbon sink might play an important role in the global carbon cycle.

5. Conclusions

Natural vegetation restoration and tree plantation are the two most important measures for ecosystem restoration on the Loess Plateau. These restoration measures have produced completely different vegetation landscapes in DZG (grassland) and YJG (forestland) after 60 years of vegetation restoration and construction. The results of this study showed that the two ecosystems had completely different mechanisms of SOC and SIC storage and distribution. The naturally restored grassland stored more SOC than the artificial forestland, and the two ecosystems had different mechanisms of surface soil carbon accumulation. In contrast to the results for SOC, the SIC results showed that the grassland stored less SIC than the forestland, incorrectly indicating that the forestland has a greater potential as an SIC sink than the grassland. The $\delta^{13}\text{C}_{\text{SIC}}$ values indicate that the grassland generates more secondary carbonate than does the forestland and that the apparent SIC deficit of the grassland is most likely the result of DIC transport to the rivers. DIC transport and further sedimentation could produce a large potential carbon sink. Accordingly, we preliminarily judge that naturally restored grassland is more beneficial than tree plantation to soil surface SIC and SOC sequestration on the Chinese Loess Plateau.

Conflict of interest

This study has no conflict of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2014.03.105>. These data include Google map of the most important areas described in this article.

References

- Alewel C, Giesler R, Klaminder J, Leifeld J, Rollog M. Stable carbon isotopes as indicators for environmental change in peats. *Biogeosciences* 2011;8:1769–78.
- Bao ST. Chemical analysis for agricultural soil. 3rd ed. Beijing: China Agriculture Press; 1999 [in Chinese].
- Batjes NH. Total carbon and nitrogen in soils of the world. *Eur J Soil Sci* 1996;47(2): 151–63.

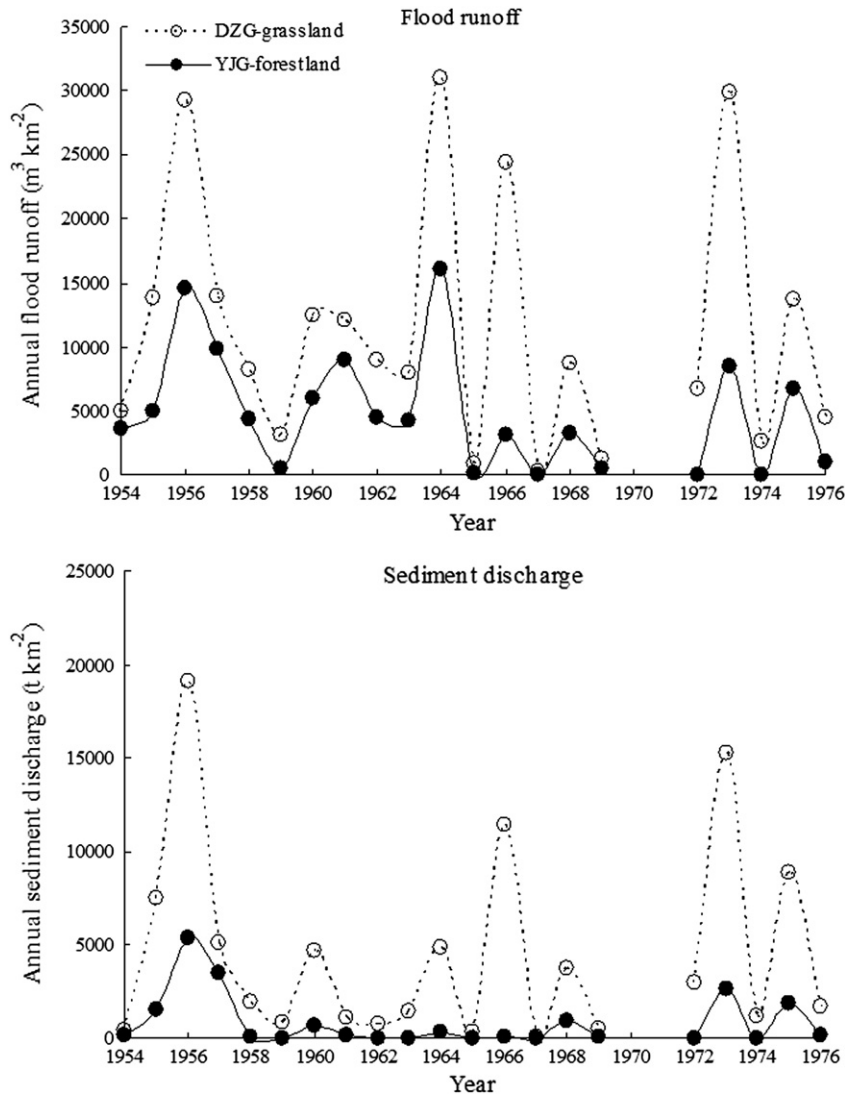


Fig. 9. Annual runoff from 1954 to 1976 in the DZG-grassland and the YJG-forestland. Data extracted from Li (2006).

- Bird MI, Pousai P. Variations of $\delta^{13}\text{C}$ in the surface soil organic carbon pool. *Glob Biogeochem Cycles* 1997;11(3):313–22.
- Boutton TW. Stable carbon isotope ratios of natural materials. II. Atmospheric, terrestrial, marine, and freshwater environments. In: Coleman DC, Fry B, editors. *Carbon isotope techniques*. New York: Academic Press; 1991. p. 173–85.
- Canadell JG, Le Quéré C, Raupach MR, Field CB, Buitenhuis ET, Ciais P, Conway TJ, Gillett NP, Houghton RA, Marland G. Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proc Natl Acad Sci* 2007;104:8866–18870.
- Cao JJ, Zhu CS, Chow JC, Liu WG, Han YM, Watson JG. Stable carbon and oxygen isotopic composition of carbonate in fugitive dust in the Chinese Loess Plateau. *Atmos Environ* 2008;42:9118–22.
- Cao S, Wang G, Chen L. Questionable value of planting thirsty trees in dry regions. *Nature* 2010;465:31.
- Cao S, Chen L, Shankman D, Wang C, Wang X, Zhang H. Excessive reliance on afforestation in China's arid and semi-arid regions: lessons in ecological restoration. *Earth-Sci Rev* 2011;104:240–5.
- Cerling TE, Quade J, Wang Y, Bowman JR. Carbon isotopes in soils and palaeosols as ecology and palaeoecology indicators. *Nature* 1989;341:138–9.
- Chang R, Fu B, Liu G, Liu S. Soil carbon sequestration potential for "Grain for Green" project in Loess Plateau, China. *Environ Manage* 2011;48:1158–72.
- Chang R, Fu B, Liu G, Wang S, Yao X. The effects of afforestation on soil organic and inorganic carbon: a case study of the Loess Plateau of China. *Catena* 2012;95:145–52.
- Chazdon RL. Beyond deforestation: restoring forests and ecosystem services on degraded lands. *Science* 2008;320:1458–60.
- Chen LD, Gong J, Fu BJ, Huang ZL, Huang YL, Gui LD. Effect of land use conversion on soil organic carbon sequestration in the loess hilly area, loess plateau of China. *Ecol Res* 2007;22:641–8.
- Ciais P, Schelhaas MJ, Zaehle S, et al. Carbon accumulation in European forests. *Nat Geosci* 2008;1:425–9.
- Conant RT, Paustian K, Elliott ET. Grassland management and conversion into grassland: effects on soil carbon. *Ecol Appl* 2001;11:343–55.
- Das A, Krishnaswami S, Bhattacharya SK. Carbon isotope ratio of dissolved inorganic carbon (DIC) in rivers draining the Deccan Traps, India: sources of DIC and their magnitudes. *Earth Planet Sci Lett* 2005;236:419–29.
- Ehleringer JR, Buchmann N, Flanagan LB. Carbon isotope ratios in belowground carbon cycle processes. *Ecol Appl* 2000;10(2):412–22.
- Emmerich WE. Carbon dioxide fluxes in a semiarid environment with high carbonate soils. *Agric For Meteorol* 2003;116:91–102.
- Feng X, Fu B, Nan Lu, Zeng Y, Wu B. How ecological restoration alters ecosystem services: an analysis of carbon sequestration in China's Loess Plateau. *Sci Rep* 2013;3:2846. <http://dx.doi.org/10.1038/srep02846>.
- Friedli H, Lotscher H, Oeschger H, Siegenthaler U, Stauffer B. Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries. *Nature* 1986;324:237–8.
- Gu ZY. The carbonate isotopic composition of the loess-paleosol sequence and its implication of paleoclimatic change. *Chin Sci Bull* 1991;36:1979–83.
- Guo LB, Gifford RM. Soil carbon stocks and land use change: a meta analysis. *Glob Chang Biol* 2002;8:345–60.
- Houghton RA. Why are estimates of the terrestrial carbon balance so different? *Glob Chang Biol* 2003;9:500–9.
- Houghton RA, Hackler JL, Lawrence KT. The U.S. carbon budget: contributions from land-use change. *Science* 1999;285:574–8.
- Huang MB, Kang SZ, Li YS. A comparison of hydrological behaviors of forest and grassland watersheds in gully region of the Loess Plateau. *J Nat Resour* 1999;14(3):226–31. [in Chinese].
- Huang Y, Sun WJ, Zhang W, Yu YQ. Changes in soil organic carbon of terrestrial ecosystems in China: a mini-review. *Sci China Life Sci* 2010;53(7):766–75.
- Huang L, Liu J, Shao Q, Xu X. Carbon sequestration by forestation across China: past, present, and future. *Renew Sust Energ Rev* 2012;16:1291–9.
- Karim A, Veizer J. Weathering processes in the Indus River Basin: implications from riverine carbon, sulfur, oxygen, and strontium isotopes. *Chem Geol* 2000;170:153–77.

- Lal R. Soil carbon sequestration in natural and managed tropical forest ecosystems. *J Sustainable For* 2004;21(1):1–30.
- Lal R. Soil carbon sequestration impacts on global climate change and food security. *Science* 2004;304:1623–7.
- Lal R, Kimble JM. Pedogenic carbonates and the global carbon cycle. In: Lal R, Kimble JM, Eswaran H, Stewart BA, editors. *Global change and pedogenic carbonate*. Boca Raton, FL: CRC Press; 2000. p. 1–14.
- Lapensis AG, Lawrence GB, Bailey SW, et al. Climatically driven loss of calcium in steppe soil as a sink for atmospheric carbon. *Glob Biogeochem Cycles* 2008;22. <http://dx.doi.org/10.1029/2007GB003077>.
- Leavitt SW, Paul EA, Kimball BA, et al. Carbon isotope dynamics of CO₂-enriched FACE cotton and soils. *Agric For Meteorol* 1994;70:87–101.
- Li M. The influence of vegetation change on hydrologic factor in Nanxiaohegou. Dissertation Xi'an University of Technology; 2006 [in Chinese].
- Li SL, Liu CQ, Lang YC, Tao FX, Zhao ZQ, Zhou ZH. Stable carbon isotope biogeochemistry and anthropogenic impacts on karst ground water, Zunyi, Southwest China. *Aquat Geochem* 2008;14:211–21.
- Li G, Chen J, Chen Y. Primary and secondary carbonate in Chinese loess discriminated by trace element composition. *Geochim Cosmochim Acta* 2013;103:26–35.
- Liu Z, Dreybrodt W, Wang H. A new direction in effective accounting for the atmospheric CO₂ budget: considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. *Earth-Sci Rev* 2010;99:162–72.
- Liu Z, Shao M, Wang Y. Effect of environmental factors on regional soil organic carbon stocks across the Loess Plateau region, China. *Agric Ecosyst Environ* 2011;142:184–94.
- Lü Y, Fu B, Feng X, et al. A policy-driven large scale ecological restoration: quantifying ecosystem services changes in the Loess Plateau of China. *PLoS ONE* 2012;7(2):e31782. <http://dx.doi.org/10.1371/journal.pone.0031782>.
- Lugo AE, Brown S. Management of tropical soils as sinks or sources of atmospheric carbon. *Plant Soil* 1993;149:27–41.
- Mi N, Wang SQ, Liu JY, Yu GR, Zhang WJ, Jobbágy E. Soil inorganic carbon storage pattern in China. *Glob Chang Biol* 2008;14:2380–7.
- Nadelhoffer KJ, Fry B. Controls on natural nitrogen-15 and carbon-13 abundances in forests soil organic matter. *Soil Sci Soc Am J* 1988;52:1633–40.
- Ning YF, Liu WG, An ZS. Variation of soil $\delta^{13}\text{C}$ values in Xifeng loess-paleosol sequence and its paleoenvironmental implication. *Chin Sci Bull* 2006;51(11):1350–4. [in Chinese].
- Pan Y, Birdsey RA, Fang JY, et al. A large and persistent carbon sink in the world's forests. *Science* 2011;333:988–93.
- Piao SL, Fang JY, Ciais P, Peylin P, Huang Y, Sitch S, et al. The carbon balance of terrestrial ecosystems in China. *Nature* 2009;458:1009–13.
- Qiu L, Wei X, Zhang X, Cheng J. Ecosystem carbon and nitrogen accumulation after grazing exclusion in semiarid grassland. *PLoS ONE* 2013;8(1):e55433. <http://dx.doi.org/10.1371/journal.pone.0055433>.
- Rao Z, Zhu Z, Chen F, Zhang J. Does $\delta^{13}\text{C}_{\text{carb}}$ of the Chinese loess indicate past C3/C4 abundance? A review of research on stable carbon isotopes of the Chinese loess. *Quat Sci Rev* 2006;25:2251–7.
- Renforth P, Manning DAC, Lopez-Capel E. Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide. *Appl Geochem* 2009;24:1757–64.
- Schimel DS, House JI, Hibbard KA, et al. Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems. *Nature* 2001;414:169–72.
- Schlesinger WH. Carbon storage in the caliche of arid soils: a case study from Arizona. *Soil Sci* 1982;133:247–55.
- Schlesinger WH. The formation of caliche in soils of the Mojave Desert, California. *Geochim Cosmochim Acta* 1985;49:57–66.
- Schlesinger WH. Carbon sequestration in soils. *Science* 1999;284:2095.
- Schlesinger WH, Belpat J, Marion G. On carbon sequestration in desert ecosystems. *Glob Chang Biol* 2009;15:1488–90.
- Scholes RJ, Noble IR. Storing carbon on land. *Science* 2001;294:1012–3.
- Stone R. Have desert researchers discovered a hidden loop in the carbon cycle? *Science* 2008;320:1409–10.
- Tate KR, Scott NA, Ross DJ, Parshotam A, Claydon JJ. Plant effects on soil carbon storage and turnover in a montane beech (*Nothofagus*) forest and adjacent tussock grassland in New Zealand. *Aust J Soil Res* 2000;38:685–98.
- Trolier M, White JWC, Tans PP, Masarie KA, Gemery PA. Monitoring the isotopic composition of atmospheric CO₂: measurements from the NOAA Global Air Sampling Network. *J Geophys Res* 1996;101:25897–916.
- Tu XM, Cao JJ, Han YM, Shen ZX, Zhang BC. Storage and spatial distribution of organic and inorganic carbon in the topsoil of Loess Plateau. *J Arid Land Resour Environ* 2012;26(2):114–8. [in Chinese].
- Wang Y, Cao S. Carbon sequestration may have negative impacts on ecosystem health. *Environ Sci Technol* 2011;45:1759–60.
- Wang HS, Huang MB, Zhang L. Impacts of re-vegetation on water cycle in a small watershed of the Loess Plateau. *J Nat Resour* 2004;19(3):344–50. [in Chinese].
- Wang YQ, Zhang XY, Arimoto R, Cao JJ, Shen ZX. Characteristics of carbonate content and carbon and oxygen isotopic composition of north China soil and dust aerosol and its application to tracing dust sources. *Atmos Environ* 2005;39:2631–42.
- Wang Y, Li Y, Ye X, Chu Y, Wang X. Profile storage of organic/inorganic carbon in soil: from forest to desert. *Sci Total Environ* 2010b;408:1925–31.
- Wang Y, Fu B, Lü Y, Chen L. Effects of vegetation restoration on soil organic carbon sequestration at multiple scales in semi-arid Loess Plateau, China. *Catena* 2011;85:58–66.
- Watson RT, Noble IR, Bolin B, Ravindranath NH, Verardo DJ, Dokken DJ. A special report of the intergovernmental panel on climate change: land use, land-use change and forestry. UK: Cambridge University Press; 2000.
- Wei XR, Shao MA, Fu XL, Horton R, Li Y, Zhang XC. Distribution of soil organic C, N and P in three adjacent land use patterns in the northern Loess Plateau, China. *Biogeochemistry* 2009;96:149–62.
- Wei J, Cheng J, Li W, Liu W. Comparing the effect of naturally restored forest and grassland on carbon sequestration and its vertical distribution in the Chinese Loess Plateau. *PLoS ONE* 2012;7(7):e40123. <http://dx.doi.org/10.1371/journal.pone.0040123>.
- Wen QZ. Loess geochemistry in China. Beijing: China Science Press; 1989 [in Chinese].
- Woodbury PB, Heath LS, Smith JE. Effects of land use change on soil carbon cycling in the conterminous United States from 1900 to 2050. *Glob Biogeochem Cycles* 2007;21:GB3006. <http://dx.doi.org/10.1029/2007GB002950>.
- Wu H, Guo Z, Gao Q, Peng C. Distribution of soil inorganic carbon storage and its changes due to agricultural land use activity in China. *Agric Ecosyst Environ* 2009;129:413–21.
- Wynn JG, Harden JW, Fries TL. Stable carbon isotope depth profiles and soil organic carbon dynamics in the lower Mississippi Basin. *Geoderma* 2006;131:89–109.
- Xie J, Li Y, Zhai C, Li C, Lan Z. CO₂ absorption by alkaline soils and its implication to the global carbon cycle. *Environ Geol* 2009;56:953–61.
- Yin R, Sedjo R, Liu P. The potential and challenges of sequestering carbon and generating other services in China's forest ecosystems. *Environ Sci Technol* 2010;44:5687–8.
- Yu G, Wang S, Chen P, Li Q. Isotope tracer approaches in soil organic carbon cycle research. *Adv Earth Sci* 2005;20(5):568–77. [in Chinese].
- Zhan C, Cao J, Han Y, Huang S, Tu X, Wang P, et al. Spatial distributions and sequestrations of organic carbon and black carbon in soils from the Chinese loess plateau. *Sci Total Environ* 2013;465:255–66.
- Zhang R. Spatial distribution of soil inorganic carbon density, stock and its affecting factors in the Loess plateau. Dissertation Chinese Academy of Sciences; 2012 [in Chinese].
- Zhao G, Mu X, Wen Z, Wang F, Gao P. Soil erosion, conservation, and eco-environment changes in the Loess Plateau of China. *Land Degrad Dev* 2013;24:499–510.
- Zhou P, Wen A, Zhang X, He X. Soil conservation and sustainable eco-environment in the Loess Plateau of China. *Environ Earth Sci* 2013;68:633–9.