

Neof ormation of pedogenic carbonates by irrigation and fertilization and their contribution to carbon sequestration in soil



Mansoor A. Bughio^{a,f}, Panlei Wang^a, Fanqiao Meng^{a,*}, Chen Qing^a, Yakov Kuzyakov^{b,e},
Xiujun Wang^c, S.A. Junejo^d

^a College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, China

^b Department of Soil Science of Temperate and Boreal Ecosystems, Department of Agricultural Soil Science, Georg-August-Universität Göttingen, Büsgenweg 2, 37077 Göttingen, Germany

^c Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20740, USA

^d Department of Geography, University of Sindh Jamshoro, Pakistan

^e Institute of Environmental Sciences, Kazan Federal University, Kazan, Russia

^f Agriculture Extension, Agriculture Department, Government of Sindh, Pakistan

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ABSTRACT

The impact of land use change and farming management on soil organic carbon (SOC) and soil inorganic carbon (SIC), particularly pedogenic carbonates (PC), was assessed in a semi-humid region of China. The SOC and SIC content and stocks were measured, and $\delta^{13}\text{C}$ values were used to calculate the percentage of PC and lithogenic carbonates (LC) in the total SIC. Over the 39-year period, organic fertilizers at high and low rates (OFH and OFL), mineral fertilizers (MF), and a control site without fertilizers (CK) showed an increase of PC compared to a natural fallow plot (F). The main pathway of SIC accumulation was the neof ormation of pedo-atmogenic carbonates contributing to C sequestration of at least 0.38, 0.27, 0.23, and 0.12 $\text{Mg C ha}^{-1} \text{ yr}^{-1}$ for the OFH, OFL, MF, and CK treatments, respectively. The LC stock remained similar in all treatments except for the CK, where LC was significantly lower than all of the other treatments which suggested dissolution. An increase in OC stocks in response to organic fertilization was not limited to the surface soil, but it continued down the soil profile to a depth of 160 cm. The maximum potential for neof ormation of PC depends on Ca^{2+} and Mg^{2+} availability; in this study these cations were provided by irrigation water. However, organic and mineral fertilizers modify this potential. Without organic and mineral fertilization, the PC formed at the expense of dissolution and re-precipitation of LC, even when substantial quantities of Ca^{2+} and Mg^{2+} were present in the soil. Our experimental results indicate that the neof ormation of PC should be considered during estimation of soil carbon stocks and sequestration for the development of optimal fertilization, irrigation and land use practices.¹³

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1. Introduction

Atmospheric CO_2 concentrations have increased by 31% since the 1750s due to the combustion of fossil fuel and land use changes. This has necessitated the identification of mitigation strategies in response to global warming and climate change (Lal, 2004). Agricultural land occupies 37% of the earth's land surface and it is believed that agriculture could offset, at full biophysical potential, about 20% of the total annual CO_2 emissions (Smith et al., 2008). The impact of agricultural management on soil organic carbon (SOC) is relatively well known. However, the effect on soil inorganic carbon (SIC), which is another potentially important carbon (C) sequestration mechanism, to date has been poorly studied (Lal and Kimble, 2000), especially in soils under semi-humid climate. SIC sequestration involves the transfer of atmospheric CO_2 into the soil C pool through the formation of secondary carbonates

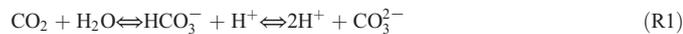
(Lal, 2007). The turnover time of SIC is much longer (85,000 years, Schlesinger, 1985) than that of SOC (200–1200 years, Trumbore, 2000). The global SIC pool is estimated to be about two-thirds of the SOC pool to a depth of 1 m (Eswaran et al., 2000). As carbonate precipitation occurs at depths as deep as 2 to 3 m, the contribution of SIC to global C stocks is greater when deeper soil profiles are evaluated (Díaz-Hernández et al., 2003). Carbonates can be classified as primary or lithogenic (mainly from the parent material) or secondary/pedogenic (newly developed as a result of dissolution and recrystallization of primary carbonates and other soil forming processes) (Kuzyakov et al., 2006). The depth of pedogenic carbonate formation increases with increasing mean annual precipitation, with shallow formations in arid climates and deep formations in semi-arid and sub-humid climates (Gocke et al., 2012; Lal, 2007).

Flows of inorganic carbon in the biosphere have three dominant processes: weathering of silicate minerals (Sommer et al., 2006), carbonate dissolution, and pedogenic carbonate formation (Sanderman, 2012). The first two processes are very slow-acting on geologic time scales, and they have limited C sequestration potential in agro-ecosystems.

* Corresponding author.

E-mail address: mengfq@cau.edu.cn (F. Meng).

Pedogenic carbonate formation, however, is more active in agricultural soils. Upon dissolution, CO₂ in soil forms carbonic acid that precipitates as carbonates of Ca²⁺ and Mg²⁺ (Lal, 2004). The main steps in the pedogenic carbonate formation process are shown in Reactions (1), (2), and (3) (for simplicity, only CaCO₃ is presented here):



Pedogenic carbonates can be further divided into pedo-lithogenic and pedo-atmogenic carbonates, depending on the sources of their constituents (Monger and Martinez-Rios, 2002). Pedo-lithogenic carbonates are formed from the dissolution and re-precipitation of pre-existing lithogenic carbonates, which have no net C sequestration. In contrast, pedo-atmogenic carbonates are created by neoformation from exogenous sources of Ca²⁺ and contribute to net C sequestration (Mikhailova and Christopher, 2006; Monger and Martinez-Rios, 2002; Monger et al., 2015). Exogenous sources of Ca²⁺ include weathering of Ca²⁺ silicates (Sommer et al., 2006), atmospheric additions of non-carbonate Ca²⁺, irrigation, and applications of biosolids and mineral fertilizers (Lal, 2007; Mikhailova and Christopher, 2006; Monger and Martinez-Rios, 2002). A supply of Ca²⁺ ions is a prerequisite for the formation of pedogenic carbonates (Schlesinger et al., 2009). Primary mineral weathering is expected to play an important role in supplying Ca²⁺ and Mg²⁺ in areas of intensive agriculture where biological activity is greater than that of undisturbed soils (Kelly et al., 1998; Mikhailova and Christopher, 2006).

Isotopic signatures of δ¹³C are widely used to distinguish between pedogenic and lithogenic carbonates in soils (Eshel et al., 2007; Landi et al., 2003; Pustovoytov, 2002). CO₂ in soil will affect the δ¹³C value of pedogenic carbonate, and during periods of microbial activity (adequate moisture and temperature) the isotopic ratios of soil CO₂ generally reflect those of the soil organic matter (Rabenhorst et al., 1984). The relative contributions of C3 (δ¹³C ≈ -27‰) versus C4 (δ¹³C ≈ -13‰) plant types control the δ¹³C value of organic matter in the soil (Midwood and Boutton, 1998). Consequently, pedogenic carbonates have more negative δ¹³C values, while the δ¹³C values for ancient carbonates have a mean value of 0‰ (Liu et al., 2011; Rabenhorst et al., 1984; P. Wang et al., 2014; X.J. Wang et al., 2014; West et al., 1988). Using these isotopic values it is possible to estimate the proportions of pedogenic and lithogenic carbonates in total SIC (Gocke et al., 2011; Landi et al., 2003; Salomons and Mook, 1976).

China has approximately 138 million hectares of cropland (NSS, 1998), and SIC represents 40% of the entire C stored in China's soils (Mi et al., 2008). Irrigation, mineral fertilization, and organic amendments are the main practices to increase land productivity and fertility of the agricultural soils. The effects of these practices on PC stock change, however, are rarely investigated, especially at deeper soil depths. We hypothesized that high inputs of Ca²⁺ or Mg²⁺ from irrigation or organic and mineral fertilizers will lead to the neoformation and accumulation of PC stocks. The objectives of this study, therefore, were: (i) to quantify soil organic and inorganic C pools as affected by agricultural practices to a soil depth of 160 cm, (ii) to further partition the SIC pool to LC and PC stocks using the δ¹³C signature, (iii) to identify the pathways of PC formation and differentiating between pedo-lithogenic and pedo-atmogenic carbonates; and (iv) to compare actual and potential neoformations of pedo-atmogenic carbonates from Ca²⁺ and Mg²⁺ supplied by irrigation and fertilization.

2. Materials and methods

2.1. Site description and experimental design

The experiment was conducted at Quzhou agricultural experiment station of China Agricultural University, Hebei Province China (36°52'

N, 115°100'E). The site is approximately 37 m above sea level with an average annual temperature of 13.2 °C, ranging from a maximum of 26.8 °C in July to a minimum of -2.9 °C in January. Mean precipitation is 543 mm; the average annual evaporation is 1840 mm and the average annual sunshine duration is 2330 h. This region possesses a warm, sub-humid climate with a severely dry spring, wet summer, and dry-cold winter. The soil parent materials in the region are from the Loess soil of the Holocene (10,000 a.B.P.) (Wang et al., 2002). The main minerals in the soil are illite and smectite and the soil is classified as Fluvic Cambisol according to WRB 2014 (Meng et al., 2014; Xin and Li, 1990).

The land use at the site (saline-alkaline soils with poor drainage) changed from natural vegetation to agricultural land in 1974 (Meng et al., 2014). Naturally-occurring plant species were a mix of C3 and C4 plants, with C3 as the dominant species which mainly consisted of green burtle grass (*Setaria viridis* L.), speak grass (*Imperata cylindrica* L.), Asian hazel (*Corylus heterophylla* L.), and stipe (*Stipa grandis* L.). A plot of about 500 square meters with original plantation was intentionally reserved, undisturbed, to observe the impact of land use change and management practices on land productivity and soil quality. This natural fallow plot (F), which does not have any management practices, was used as a reference plot to compare with the farming treatments in the current study. The crop rotation was winter wheat (*Triticum aestivum* L.) followed by cotton (*Gossypium hirsutum*) between 1974 and 1993.

The long-term farming experiment was initiated in 1993 with two crops per year, i.e., winter wheat (*T. aestivum* L.) and summer maize (*Zea mays* L.). The wheat was planted in October and harvested in June, while maize was planted in June and harvested in October. Since the land use change the crop sequence has been the same for all of the treatment plots at the given time periods. The fertilization treatments included organic fertilizer (compost) containing 60% (w/w) straw (wheat straw in June, maize straw in October), 30% chicken dung, 5% cotton seed pressed trash, and 5% bran (mainly from wheat). The organic fertilizer was applied at a rate of 15 Mg ha⁻¹ (OFH) and 7.5 Mg ha⁻¹ (OFL) and it was incorporated into the soil by cultivation. For the MF treatment, the mineral fertilizer consisted of ammonium bicarbonate (750 kg ha⁻¹), urea (300 kg ha⁻¹), and calcium super-phosphate (750 kg ha⁻¹). The fertilizers were applied in June and October each year prior to the sowing of the crops. The unfertilized plots (CK) were cultivated and harvested for wheat and maize in a similar manner as the OFL, OFH, and MF plots. The different treatments were arranged in a complete randomized block design with a plot size of 10.5 × 3 m per treatment. Groundwater was used for irrigation (480 mm yr⁻¹) for all farming treatment plots (i.e., OFH, OFL, MF and CK). The water contained 0.23 g Ca²⁺ L⁻¹ and 0.14 g Mg²⁺ L⁻¹. Soil pH at the 0–20 cm depth was 7.65, 7.57, 7.6, 7.58 and 8.3 for CK, MF, OFL, OFH and F, respectively.

2.2. Soil sampling and analysis

In June 2013, after the wheat harvest, composite soil samples were collected using a 35-mm soil probe to a depth of 160 cm, at 20-cm intervals and subsequently five cores of respective depths from each replicate (3 replicates from each treatment) were mixed. Samples were air-dried, crushed, and passed through a 2.0 mm sieve. Subsamples were ground for pH, SIC, SOC, and isotopic analyses. Bulk density was measured by selecting a 160 cm deep soil profile for each treatment. Soil samples for SOC analysis were ground and passed through a 0.15 mm sieve and soaked in 0.5 M HCl for 12 h in order to remove carbonates. A pre-experiment was undertaken to ensure that the carbonates were completely removed in an appropriate concentration of HCl with a suitable treatment time (P. Wang et al., 2014; X.J. Wang et al., 2014). To ensure all of the excess acid had been removed the soil was washed with de-ionized water and repeated centrifugation until the pH of the solution was neutral. The soil was then oven dried at 60 °C. The acidified soil samples were pulverized and combusted at 1020 °C with a constant flow of helium carrying pure oxygen to ensure

completed oxidation of organic materials. Production of CO₂ was determined by a thermal conductivity detector using a NC soil analyzer flash 2000 (Thermo Fisher Scientific, USA). Total soil carbon was measured in a similar way as SOC, though without the removal of the carbonates. SIC was calculated as the difference between total soil carbon and SOC.

Isotopic composition of SOC for acidified soils was determined using an isotope ratio mass spectrometer DELTA plus (Thermo Fisher Scientific, USA) at the Chinese Academy of Agricultural Sciences, Beijing. The CO₂ for δ¹³C measurements of SIC was collected from a vacuum system where soil samples were reacted with 100% H₃PO₄ for 3 h at 70 °C. The collected CO₂ was then analyzed for isotopic analysis using a mass spectrometer DELTA V Advantage (Thermo Fisher Scientific, USA) located at the Third Institute of Oceanography in Xiamen, China. δ¹³C was expressed as relative to the international standard of PDB.

2.3. Calculation of SOC, SIC and PC stocks

The SOC and SIC stocks for each soil layer were calculated by adjusting soil mass for their respective bulk densities. Profile data were generated by combining average C stocks in each of the 20 cm depth increments with the data presented as SOC and SIC stocks (in Mg C ha⁻¹). The proportion of PC in total SIC was estimated by using the isotopic mass balance equation (Eq. (1)) (Salomons and Mook, 1976):

$$\%_{\text{pedogenic}} = \frac{\delta^{13}\text{C}_{(\text{SIC})} - \delta^{13}\text{C}_{(\text{par.mat})}}{\delta^{13}\text{C}_{(\text{ped.})} - \delta^{13}\text{C}_{(\text{par.mat})}} \times 100 \quad (1)$$

where δ¹³C_(SIC), δ¹³C_(par.mat), and δ¹³C_(ped.) are the stable C isotopic compositions of the inorganic carbonate in the bulk soil, parent materials, and pedogenic carbonates, respectively. The δ¹³C values for parent materials were assumed to be zero (Liu et al., 2011; Rabenhorst et al., 1984; West et al., 1988). While studying the Pedogenic carbonates at Zheng Zhou site, P. Wang et al. (2014) and X.J. Wang et al. (2014) also used an assumed value of zero for δ¹³C of the parent material which is near to our experimental site. The sensitivity analysis by them showed that variation in the δ¹³C values of parent material did not change the findings of the impact of farming measures on pedogenic carbon formation.

Pedogenic carbonate segregations were not present in the form of nodules or soft masses that could be physically isolated for isotopic analysis. Therefore, the δ¹³C values for pedogenic carbonate were estimated from the δ¹³C values of the soil organic matter using Eq. (2) (Nordt et al., 1998):

$$\delta^{13}\text{C}_{\text{pedogenic carbonate}} = \delta^{13}\text{C}_{\text{SOM}} + \Delta_{\text{CO}_2 \text{ diffusion}} + \Delta_{\text{CO}_2 - \text{CaCO}_3} \quad (2)$$

where δ¹³C_{SOM} is the measured value and Δ_{CO₂ diffusion} is the δ¹³C difference between ¹²CO₂ and ¹³CO₂ molecules with a theoretical value of +4.4‰ (Cerling, 1984; Cerling et al., 1991). The value Δ_{CO₂-CaCO₃} is the δ¹³C difference between C in CaCO₃ and CO₂ during equilibrium reactions, which is temperature dependent. The average annual temperature for the study site was 13.2 °C. By using this in Eq. (3) (Cerling, 1999) the estimated value for Δ_{CO₂-CaCO₃} was +10.27‰.

$$10^3 \ln(\Delta_{\text{CO}_2 - \text{CaCO}_3}) = 11.709 - 0.116(T) + 2.16 \times 10^{-4}(T)^2 \quad (3)$$

These values were used in Eq. (2), as follows:

$$\delta^{13}\text{C}_{\text{pedogenic carbonate}} = \delta^{13}\text{C}_{\text{SOM}} + 4.4\text{‰} + 10.27\text{‰}. \quad (4)$$

The fractionation factor is difference between the average δ¹³C values of organic matter and δ¹³C values of pedogenic carbonate, and it should range from 13.5‰ to 16.5‰ (Cerling and Quade, 1993). In the current study the fractionation factor was 14.67‰. This value is also consistent with previous studies where pedogenic carbonates were physically isolated from the subsoil (Cerling et al., 1989; Cole

and Monger, 1994; Kelly et al., 1991; Wang et al., 1993). The estimated δ¹³C values of pedogenic carbonates were then used in Eq. (1) to calculate the percentage of pedogenic carbon in total SIC. Subsequently, the pedogenic and lithogenic carbon stocks were calculated using the percentage of PC and LC in the SIC stock.

The approach employed in the current study did not trace the individual contribution of CO₂ from root respiration of different crops and decomposition of organic amendments that affected the δ¹³C of SOC and the pedogenic carbonates over time. It is presumed that root and soil respiration will be higher in the maize crop due to the longer duration of higher temperatures compared with the winter wheat growing seasons. Therefore, maize cropping might have a greater impact on the δ¹³C of SOC and pedogenic carbonate formation in the farming treatments. However, the aim of the current study was to assess the integrated impact of land use change and farming practices on SOC and SIC. The δ¹³C values of SOC/SOM used in Eq. (2) aggregated contributions of all the organic carbon inputs (crop residues, animal manure, and C3 or C4 plant residues). Consequently, δ¹³C of pedogenic carbonates which were estimated by the δ¹³C value of SOC also reflected the cumulative impact of all these contributing factors. Similarly, the variation of δ¹³C value for pedogenic carbonate in Eq. (1) only changed the proportion of PC and LC in the total SIC; it could not hide the significance of farming practices (irrigation and fertilization) in soil carbon transformation.

2.4. Statistical analysis

Statistical analysis was performed using SPSS 17.0. Multivariate ANOVA was used to estimate the effects of fertilization, soil sampling depth, and their interactions on content and δ¹³C values of SOC and SIC. The contribution of the factors and their interactions to the total variance was assessed by dividing the respective type III sum of squares by the total sum of type III sum of squares from multifactorial ANOVA. Differences between the means greater than the LSD were considered statistically significant (*P* < 0.05). Data was reported as mean ± SE.

3. Results

3.1. SOC, SIC, and TC content and stocks

In all treatments the SOC content was highest at the surface and continuously decreased with soil depth (Fig. 1). Compared to all other treatments at the 0–20 cm soil depth, the application of organic fertilizers, particularly that of the OFH treatment, significantly increased OC content. Although the SOC contents were lower further down the soil profile, these two organic fertilizer treatments contributed to higher SOC contents throughout the entire soil profile when compared with CK treatment and plot F (except at 60–100 cm for F). The SOC content between the OFH and OFL treatments were not significantly different within the soil profile.

In contrast to SOC, the SIC content increased with soil depth, and increased sharply below 140 cm (Fig. 1). The OFH treatment had a higher SIC content than other treatments across the entire soil profile, although not statistically significant due to high variances among the replicates. The lowest SIC content, to the depth of 40 cm, was found in the mineral fertilization treatment (MF).

The data for SOC, SIC and TC stocks are shown for three different soil depths: 0–20, 0–100, and 0–160 cm (Table 1). The SOC stock down to 160 cm was in the order of OFH > OFL > MF > CK > F. Over the 39 years of agricultural practices the net accumulation rates of SOC for OFH (with F as reference) for soil depths of 0–20, 0–100, and 0–160 cm were 0.29, 0.50, and 0.72 Mg C ha⁻¹ yr⁻¹, respectively. For the MF treatment, these rates were 0.09, 0.11, and 0.32 Mg C ha⁻¹ yr⁻¹, respectively. These high rates of SOC stocks highlighted the importance of assessing SOC stocks deeper in the soil profile. The SIC stock significantly increased in the OFH treatment only for 0–160 cm (1.07 Mg C ha⁻¹ yr⁻¹) and compared to plot F the increases were not significant for any other treatments.

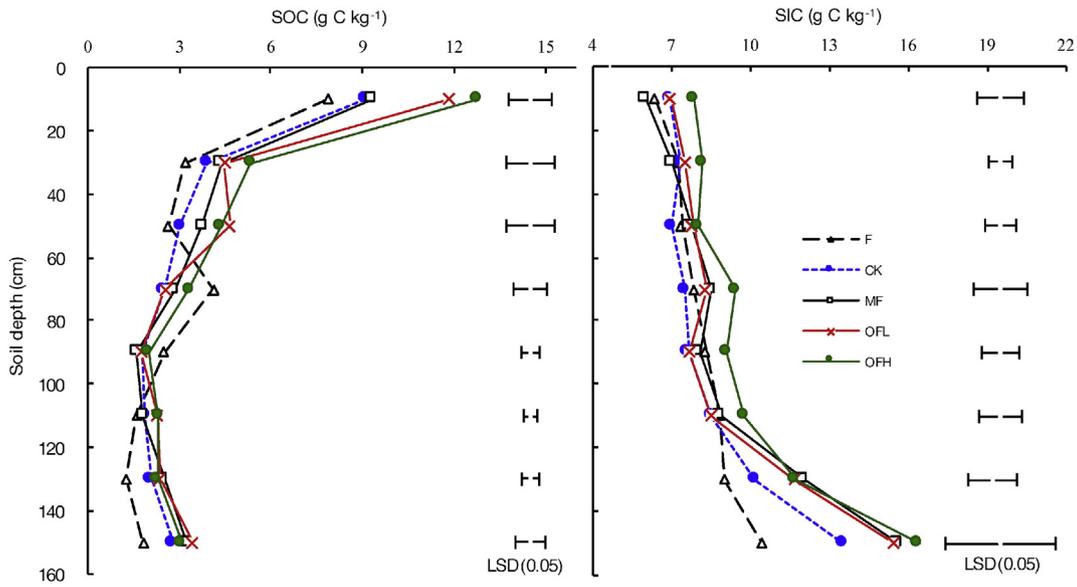


Fig. 1. Soil organic carbon (SOC, left) and inorganic carbon (SIC, right) contents affected by fertilization and land use depending on depths. F, natural fallow; CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate. Values at each depth are the means of three replicates. The bars on the right side are the LSD (0.05) for the five treatments at each depth.

The increase in both SOC and SIC in OFH treatment contributed to higher TC than the other treatments, which was significantly higher than CK and F for all of the three profile depths (Table 1).

3.2. $\delta^{13}\text{C}$ values of SOC, SIC and PC

The $\delta^{13}\text{C}$ values of SOC for F increased from -21.4% at 0–20 cm to -19.7% at the 20–40 cm depth, and then decreased gradually again to -21.7% at the 160–180 cm depth (Fig. 2). SOC of cropland soils, however, had similar $\delta^{13}\text{C}$ values (-19.0 to -19.7%) at 0–20 cm, then slightly increased to -19.3% at 40–80 cm, and decreased to about -20.6 to -21.2% until the depth of 160 cm. Plot F had lower (negative) $\delta^{13}\text{C}$ values of SOC than cropland soils from 0 to 80 cm depth, while $\delta^{13}\text{C}$ values of SOC between farming treatments were not different.

The $\delta^{13}\text{C}$ values for SIC (bulk carbonates) did not change with depth for any of the treatments from 0 to 80 cm depth (Fig. 2). However, below 80 cm, they increased with soil depth until 120 cm, and then decreased until a depth of 160 cm. CK and F had similar $\delta^{13}\text{C}$ values that were significantly lower than those of OFH, OFL, and MF down to a depth of 120 cm. Below 120 cm, however, the $\delta^{13}\text{C}$ values of SIC in plot F were significantly higher (positive) than all cropped soils.

The $\delta^{13}\text{C}$ values of PC reflected the pattern exhibited by the $\delta^{13}\text{C}$ values of SOC (Eq. (2), Fig. 2). Multivariate ANOVA analyses (Fig. 3) revealed that soil depth played the most important role in controlling SOC and SIC contents. Fertilization had a greater influence on defining the

$\delta^{13}\text{C}$ values of SOC and PC. The interaction effect between depth and fertilization was more evident on the $\delta^{13}\text{C}$ values of SIC.

3.3. Partitioning of SIC to PC and LC

The proportions of PC and LC stocks were calculated based on the $\delta^{13}\text{C}$ values (Eq. (1)) and accordingly, SIC was further divided into PC and LC pools (Table 2). To a depth of 100 cm, PC stocks decreased in the order of: CK > OFH > OFL > F > MF. CK had significantly higher PC, compared to MF and F, at depths of 0–20 cm and 0–100 cm, where MF had the lowest PC stock among all treatments. Plot F had a significantly lower PC stock, compared to all farming treatments for the total soil profile. CK had the lowest LC stock among all treatments at all soil depths, which was significantly lower than all of the other treatments at 0–100 and 0–160 cm depths. The proportion of PC in SIC was about 33% for all treatments, except for CK which had a proportion of approximately 45%.

3.4. Change of PC and LC stocks

We assumed that the PC and LC stocks in the farming treatments were originally the same as those in plot F at time zero when the saline–alkaline soil was converted to agricultural use. Hence, the losses and gains in LC and PC stocks were estimated by the differences between F and farming treatments presented in Fig. 4. This showed that the PC stocks increased at all depths with reference to F, except in the MF treatment which lost some PC at 0–20 and 0–100 cm depths.

Table 1
Soil organic carbon (SOC), soil inorganic carbon (SIC), and total carbon (TC) stocks (Mg C ha^{-1}) depending on soil depth.^a

| Treatment ^b | 0–20 cm ^c | | | 0–100 cm | | | 0–160 cm | | |
|------------------------|--------------------------|-------------|--------------|--------------|--------------|--------------|--------------|----------------|----------------|
| | SOC | SIC | TC | SOC | SIC | TC | SOC | SIC | TC |
| F | 21.0 ± 0.6c | 17.1 ± 2.9a | 38.1 ± 2.6c | 57.9 ± 2.7c | 108.6 ± 2.3a | 166.5 ± 0.4b | 71.3 ± 2.7d | 189.4 ± 8.2b | 260.7 ± 9.2c |
| CK | 25.2 ± 0.9b | 19.2 ± 1.4a | 44.4 ± 1.0bc | 58.8 ± 1.5c | 106.8 ± 6.3a | 165.6 ± 7.4b | 77.9 ± 1.3cd | 198.6 ± 10.0ab | 276.5 ± 11.0bc |
| MF | 24.6 ± 1.3bc | 15.8 ± 0.1a | 40.4 ± 1.3cd | 62.3 ± 4.3bc | 108.6 ± 3.3a | 170.8 ± 1.4b | 83.8 ± 4.5bc | 212.6 ± 3.2ab | 296.3 ± 1.4ab |
| OFL | 31.0 ± 1.4a | 18.3 ± 0.2a | 49.2 ± 1.3ab | 71.1 ± 3.2ab | 111.4 ± 2.6a | 182.4 ± 4.1b | 94.1 ± 3.5ab | 212.8 ± 6.1ab | 306.9 ± 9.5ab |
| OFH | 32.5 ± 1.5a ^a | 19.9 ± 1.0a | 52.4 ± 2.5a | 77.5 ± 3.8a | 123.0 ± 5.1a | 200.6 ± 8.8a | 99.5 ± 6.1a | 231.2 ± 11.6a | 330.6 ± 17.7a |

^a Values are mean ± standard error.

^b F, natural fallow; CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate.

^c Different letters within a column indicate significant differences ($P < 0.05$) between the treatments.

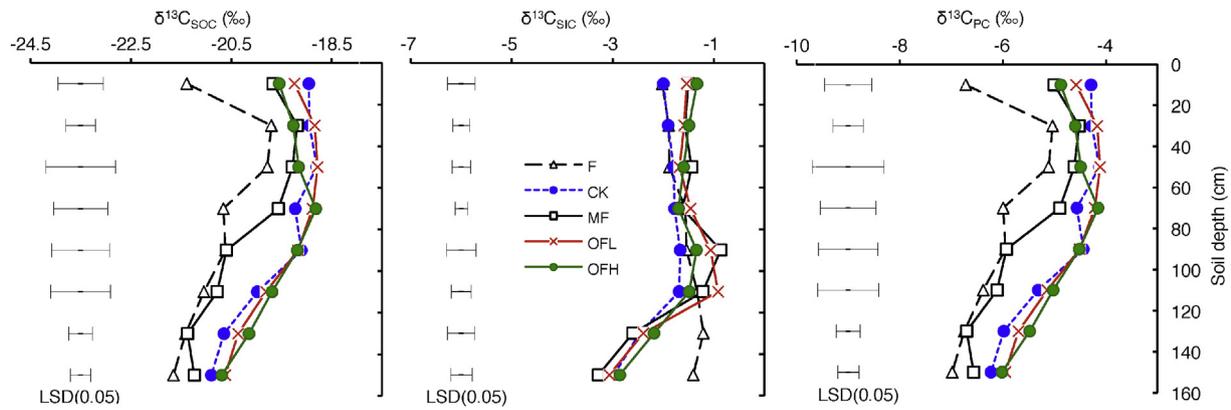


Fig. 2. Measured $\delta^{13}\text{C}$ of SOC (left) and SIC (middle), and estimated $\delta^{13}\text{C}$ of PC (right) depending on soil depth. F, natural fallow; CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate. Values at each depth are the means of the three replicates. The bars on the right side are the LSD (0.05) for the five treatments at each depth.

However, below 100 cm PC stocks in MF increased. The higher PC stocks in the CK treatment came at the expense of significant LC losses. LC in all treatments did not change significantly with reference to plot F, except in the CK treatment, where 17% of the LC was lost.

3.5. Neoformation of pedo-atmogenic carbonates

The neoformation of pedo-atmogenic carbonates due to agricultural practices over the four decades was calculated by subtracting the loss in LC from the gain in PC. The gain in LC was excluded as this did not represent neoformation of pedogenic carbon. The potential neoformation of pedo-atmogenic C was estimated with the understanding that Ca^{2+} and Mg^{2+} supplied by irrigation and fertilization could react with HCO_3^- to form CaCO_3 or MgCO_3 . These were subsequently converted to C stocks using their carbon mole fractions. The results are presented on Fig. 5. Ca^{2+} and Mg^{2+} supplied by irrigation since the change in land use at the site could potentially lead to the accumulation of approximately 27 Mg pedo-atmogenic C ha^{-1} . However, only 34% of this potential was actualized in the CK treatment. In other treatments, Ca^{2+} and Mg^{2+} supplied by 20 years of fertilization and 39 years of irrigation could potentially accumulate around 29, 30, and 33 Mg pedo-atmogenic C ha^{-1} in the MF, OFL, and OFH treatments, respectively. From this potential accumulation 61%, 70%, and 90% was actualized, respectively (Fig. 5).

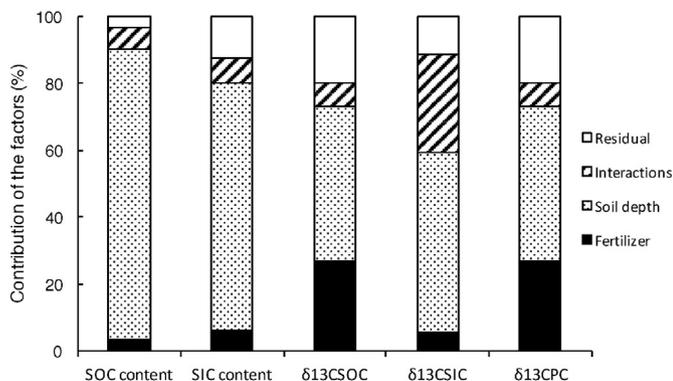


Fig. 3. Contributions of two factors: fertilization and soil sampling depth and their interactions to the variance in contents of SOC and SIC and $\delta^{13}\text{C}$ values of SOC, SIC and PC. Residual depicts the variance unexplained by either factor or interactions.

4. Discussion

4.1. Effects of land use change and farming practices on SIC and SOC stocks

The increase of SOC by organic fertilization (Fig. 1) has been confirmed by previous studies, for example Angers and N'dayegamiye (1991), Gerzabeck et al. (2001), and Liang et al. (2012). SOC increase is due to both C additions into soil aggregates directly from organic fertilizers (Chen et al., 2009) and indirectly by increased above- and below-ground biomass resulting from improved crop yields (Whalen and Chang, 2002). The binding of soil particles and the formation of organo-mineral complexes through the actions of polysaccharides, aliphatic and aromatic compounds are also promoted by organic fertilizers (Awad et al., 2012; Tisdall and Oades, 1982). An increase in Ca^{2+} in soils supplied by organic fertilizers and irrigation is also crucial for the stabilization of SOM and aggregates (Six et al., 2004). Increased organo-mineral complexes and soil aggregation will reduce the microbial decomposition of SOC (Awad et al., 2013), thereby increasing its sequestration. The significant increase in SOC stock through the soil profile to the depths of 100 and 160 cm by OFH, compared to F, MF, and CK treatments (Table 1), can be attributed to improved soil porosity and aeration which promoted water penetration and deep growth of crop roots. Organic carbon input into the subsoil mainly occurs in dissolved form (DOC) following preferential flow pathways, as above-ground or root litter and exudates move down along root channels, and through bioturbation (Rumpel and Kögel-Knabner, 2011). The net OC sequestration in OFH treatment, with reference to F over 39 years of intensive agriculture, was 0.72 and 0.29 Mg C $\text{ha}^{-1} \text{yr}^{-1}$ at depths of 0–160 and 0–20 cm, respectively. These results confirm the findings of Boddey et al. (2010), Fontaine et al. (2007) and Harper and Tibbett (2013). A large proportion of subsoil OC is believed to be stable over long periods of time, and this has been confirmed by the high radiocarbon age of the subsoil organic matter (Paul et al., 1997). Subsoil OC, therefore, may be even more important for C sequestration than topsoil OC (Rumpel and Kögel-Knabner, 2011).

4.2. Effects of land use change and farming practices on $\delta^{13}\text{C}$ values of SOC and SIC

The $\delta^{13}\text{C}$ values of SOC in plot F and the farming treatments were reflective of mixed C3 and C4 plantation. However, the more negative $\delta^{13}\text{C}$ values of SOC for plot F, compared to the farming treatments throughout the soil profile (Fig. 2), are reflective of C3 as the dominant vegetation. More positive $\delta^{13}\text{C}$ values of SOC exhibited by farming treatments represent the intensive mixed cropping of C3 and C4 plants, where the C4

Table 2
Stocks (Mg C ha⁻¹) of pedogenic carbon (PC) and lithogenic carbon (LC) depending on soil depth.^a

| Treatment ^b | 0–20 cm ^c | | 0–100 cm | | 0–160 cm | |
|------------------------|-------------------------|--------------|---------------|-------------|--------------|--------------|
| | PC | LC | PC | LC | PC | LC |
| F | 5.4 ± 1.6b | 11.6 ± 1.8ab | 35.0 ± 1.9bc | 73.6 ± 3.9a | 51.4 ± 3.4b | 138.0 ± 6.1a |
| CK | 8.9 ± 1.0a | 10.3 ± 2.2b | 45.4 ± 4.4a | 61.4 ± 3.4b | 83.6 ± 11.4a | 115.1 ± 5.0b |
| MF | 4.8 ± 0.6b | 11.1 ± 0.7ab | 31.3 ± 2.8c | 77.3 ± 1.7a | 71.8 ± 3.6a | 140.8 ± 1.4a |
| OFL | 6.2 ± 0.5ab | 12.1 ± 0.4ab | 38.3 ± 1.4abc | 73.1 ± 1.4a | 79.4 ± 5.3a | 133.4 ± 1.8a |
| OFH | 5.5 ± 0.1b ^a | 14.5 ± 1.0a | 41.5 ± 2.7ab | 81.6 ± 5.3a | 85.4 ± 4.3a | 145.8 ± 8.2a |

^a Values are mean ± standard error.

^b F, natural fallow; CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate.

^c Different letters within a column indicate significant differences (*P* < 0.05) between the treatments.

plants have influenced δ¹³C values more profoundly compared with plot F.

Unlike plot F, the sharp decrease in the δ¹³C value of SIC from the depths of 120–160 cm (Fig. 2) in all of the farming treatments coincided with the increase in SIC content in the soil profile at the same depths (Fig. 1). This suggests that there was neoformation of pedogenic carbonates at these depths, which were influenced by biogenic CO₂ from root respiration and decomposition of below-ground plant materials and added organic residues. The significant positive δ¹³C of SIC in plot F at similar depths show that the pedogenic carbonates were not affected by the biogenic CO₂ sources since the change in land use at the site.

The similar δ¹³C values of SIC in CK and F to a depth of 100 cm revealed that the pedogenic carbonate in the CK treatment had a pedo-lithogenic origin reflected by the original δ¹³C signature of their constituent materials exhibited in plot F. In the case of dissolution and reprecipitation of pedogenic carbonate almost no change in δ¹³C values will occur (Magaritz and Amiel, 1981)

4.3. Pathways of PC formation and identification of pedo-lithogenic and pedo-atmogenic carbonates

In our study, the natural fallow (F) plot provided a unique opportunity to investigate the impact of human activities on the dynamics of PC and LC stocks over the 39-year period. It also helped to distinguish pedo-atmogenic carbonates from pedo-lithogenic carbonates; the former representing neoformation, and the latter representing reprecipitation of pre-existing carbonates. Pathways of PC formation in plot F were unaffected by human activities. Possible sources of Ca²⁺ and

Mg²⁺ contributed by calcium salts in soil and dry/wet deposits. As all of the farming plots, and plot F, were in the same geographical location, c. 100 m apart, these sources of Ca²⁺ and bicarbonates were received in equal quantities. The differences in PC and LC stocks in the farming treatments compared to plot F, therefore, are mainly due to agricultural practices such as irrigation, fertilization and tillage. Higher PC stocks in the CK treatment were at the expense of significant LC losses, showing their pedo-lithogenic origin (Table 2 & Fig. 4). Formations of pedo-atmogenic C in the CK treatment were also identified; however this was the least compared to all other treatments (Fig. 5). These results are in line with studies by Amundson and Smith (1988) and McCaslin and Lee-Rodriguez (1979), who reported increases in PC formation with the use of irrigation water.

The potential neo-formation of pedo-atmogenic C was mainly defined by Ca²⁺ and Mg²⁺ supplied from irrigation water. The mineral fertilization in MF and organic fertilization in the OFL and OFH treatments contributed small amount of the total Ca²⁺ and Mg²⁺ (Fig. 5). Neoformation of pedo-atmogenic carbon, however, was more profound in the OFH treatment, followed by the OFL and MF compared to plot F and the CK treatment (Fig. 5). Irrigation and fertilization caused an obvious increase in plant biomass production in the farming treatments relative to the plot F, resulting in increased root and microbial respiration. This led to increased soil CO₂ levels and the formation of pedogenic carbonates. Our results indicated that, although the sources of Ca²⁺ and Mg²⁺ are a pre-requisite for the formation of pedogenic carbonates, the sources of CO₂ are also important. A strong synergistic interaction exists between SOC and pedogenic carbonates; pedogenic carbonates increased with increasing application rates of biosolids to the soil

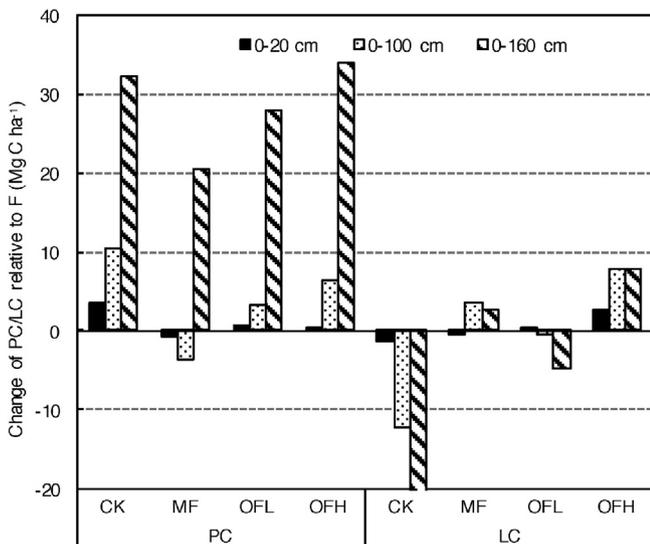


Fig. 4. Change of pedogenic carbonates (PC) and lithogenic carbonates (LC) during the 39 years, calculated as differences between management treatments and F at soil depths of 0–20, 0–100, and 0–160 cm. F, natural fallow; CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate.

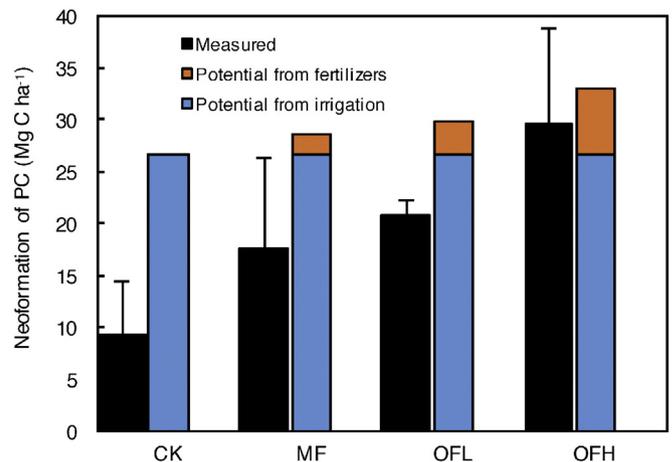


Fig. 5. Comparison between measured and the potential neo-formation of pedo-atmogenic carbonates at soil depth 0–160 cm. The potential neo-formation of pedo-atmogenic carbonates was estimated considering the Ca²⁺ and Mg²⁺ input by irrigation and fertilization that could react with HCO₃⁻ to form CaCO₃ or MgCO₃. CK, control without fertilization; MF, mineral fertilizers; OFL, organic fertilizers at low rate; OFH, organic fertilizers at high rate.

(Lal, 2004). Organic fertilization caused significant increases in above and below-ground biomass production, thereby enhancing evapotranspiration. Water loss through evapotranspiration is considered to be one of the primary mechanisms involved in the precipitation of pedogenic carbonates (Rabenhorst et al., 1984). Moreover, microorganisms play an important function in carbonate precipitation in arid soils. The supply of a substrate in the fertilization treatments enhanced the microbial activity and precipitation of carbonate in these treatments. Previous investigations on air dust across North China have indicated that it contains high levels of Ca^{2+} (Shen et al., 2009; Wang et al., 2005; Zhang and Iwasaka, 1999). This source of Ca^{2+} input may have contributed to pedo-atmogenic carbonate formation, especially in farming treatments where CO_2 concentrations were higher compared to plot F.

No significant change in LC stocks for all of the farming treatments, except for CK (Table 2, Fig. 4), indicated that pedogenic carbonate formation was independent of the dissolution of lithogenic carbonates in these treatments. Unlike other farming treatments, the neoformation of pedo-atmogenic carbon in the MF treatment occurred exclusively below 100 cm (Fig. 4). This occurrence is attributable to acidity caused by the mineral fertilization, which promoted the dissolution and downward translocation of PC.

It is also important to identify the Ca^{2+} and Mg^{2+} sources in the irrigation water to categorize the increase in pedogenic carbon stocks as a C sink or as a C source. If the Ca^{2+} source is from pre-existing carbonates in the loess parent material, then no net CO_2 has been sequestered (Monger et al., 2015). On the other hand, if the Ca^{2+} source is (1) directly from silicate minerals in the loess, (2) from silicates but stored on the exchange complex of chlorite or smectite, or (3) from silicates but stored in salts, then the carbonate is “silicatic pedogenic carbonate” and sequestration has occurred. There is evidence of chlorite and smectite minerals present in the soils of this area which contain considerable amounts of Ca^{2+} and Mg^{2+} (P. Wang et al., 2014; X.J. Wang et al., 2014). Aji et al. (2008) also reported that there are high concentrations of various Ca^{2+} and Mg^{2+} bearing salts in the ground water in this area. With intensive agricultural practices in the study area, increased weathering of these minerals and salts is believed to have contributed Ca^{2+} and Mg^{2+} to the irrigation water. Furthermore, our results also showed that the pedo-atmogenic carbonate formation was independent of dissolution and re-precipitation of pre-existing carbonates, especially in fertilized treatments. However, the possibility of carbonate dissolution from loess supplying Ca^{2+} to the irrigation water cannot be ruled out. Assuming these Ca^{2+} sources supply approximately equal amounts to the aquifer that feeds the irrigation systems, approximately half of the pedo-atmogenic carbonate is silicatic pedogenic carbonate and therefore is a C sink for at least 0.38, 0.27, 0.23, 0.12 $\text{Mg C ha}^{-1} \text{ yr}^{-1}$ for the OFH, OFL, MF, and CK treatments, respectively. More research is therefore, recommended in future to trace and quantify the different sources of Ca^{2+} and mechanisms involved in the pedogenic carbonate formation to validate the exact C sequestration potential in intensive farming systems.

5. Conclusions

SIC may strongly contribute to C sequestration, especially by the application of high rates of organic and mineral fertilizers, as well as with frequent irrigation. Our results indicate that land use change and agricultural practices not only affect SOC stocks through the whole soil profile, but also SIC stocks. The application of organic and mineral fertilizers had strong synergistic effects on neoformation of pedogenic carbonates that accumulated SIC down to depths of 160 cm. Available Ca^{2+} and Mg^{2+} supplied by irrigation, or by the application of compost and mineral fertilizers, reflect the maximum potential for the neoformation of pedogenic carbonates in agricultural soils. However, CO_2 sources are also important to actualize that potential. Without the use of organic and mineral fertilizers, the pedo-lithogenic carbonates were formed at the expense of the dissolution and re-precipitation of lithogenic carbonates, even when substantial quantities of Ca^{2+} and Mg^{2+} were present

in the soil. The increase in SOC stocks to a depth of 160 cm by fertilization is more stable and consequently more important for C sequestration than that in the topsoil. It is important, therefore, to quantify both the SOC and also pedogenic carbonates in deeper soil profiles (subsoil) to clarify the mechanisms and C dynamics affected by intensive farming practices on regional and global scales.

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