Reassessing carbon sequestration in the North China Plain via addition of nitrogen

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HIGHLIGHTS

- The SOC contents significantly increased after long-term nitrogen application, while SIC decreased.
- The measured loss of carbonate was far higher than the theoretical values of dissolution from nitrification.
- HCO_3^- / (Ca^{2+} + Mg^{2+}) ratio in soil solution was higher after N application for the 0–80 cm depth.

GRAPHICAL ABSTRACT

	SIC storage (Mg ha^{-1})		SOC storage (Mg ha^{-1})		TC storage (Mg ha^{-1})		C loss/gain efficiency in 0-60cm (g C g^{-1}N added)		
	0-60cm	0-100 cm	0-60cm	0-100 cm	0-60cm	0-100 cm	SIC	SOC	TC
CK	66.0a	138.8	53.8c	61.6c	119.8	200.4	-	-	-
N200	47.4b	125.8	65.5b	76.9b	112.9	202.7	6.2	3.4	-2.3*
N400	52.3b	124.5	69.1a	81.8a	121.4	208.9	2.3	2.6	0.3
N600	50.8b	127.2	70.7a	82.4a	121.5	209.6	1.6	1.9	0.2

ARTICLE INFO

ABSTRACT

Soil inorganic carbon (SIC) exerts a strong influence on the carbon (C) sequestered in response to nitrogen (N) additions in arid and semi-arid ecosystems, but limited information is available on in situ SIC storage and dissolution at the field level. This study determined the soil organic/inorganic carbon storage in the soil profile at 0–100 cm depths and the concentration of dissolved inorganic carbon (DIC) in soil leachate in 4 N application treatments (0, 200, 400, and 600 kg N ha^{-1} yr^{-1}) for 15 years in the North China Plain. The objectives were to evaluate the effect of nitrogen fertilizer on total amount of carbon sequestration and the uptake of atmospheric CO_2 in an agricultural system. Results showed that after 15 years of N fertilizer application the SOC contents at depths of 0–100 cm significantly increased, whereas the SIC contents significantly decreased at depths of 0–60 cm. However, the actual measured loss of carbonate was far higher than the theoretical maximum values of dissolution via protons from nitrification. Furthermore, the amount of HCO_3^- and the HCO_3^- / (Ca^{2+} + Mg^{2+}) ratio in soil leachate were higher in the N application treatments than no fertilizer input (CK) for the 0–80 cm depth. The result suggested that the dissolution of carbonate was mainly enhanced by soil carbonic acid, a process which can absorb soil or atmosphere CO_2 and less influenced by protons through the nitrification which would release CO_2. To accurately evaluate soil C sequestration under N input scenarios in semi-arid regions, future studies should include both changes in SIC storage as well as the fractions of dissolution with different sources of acids in soil profiles.

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1. Introduction

The global carbon (C) pool in the top 1 m of soil represents 2500 gigatons (Gt) and includes approximately 1550 Gt of soil organic carbon (SOC) and 950 Gt of soil inorganic carbon (SIC). The soil C pool is 3.3 times the size of the atmospheric pool (760 Gt) and 4.5 times the size of the biotic pool (560 G) (Trumbore et al., 1996; Davidson and Janssens, 2006; Luo et al., 2010). Thus, a small variation in soil C stores could lead to marked changes in the CO_2 concentration of the atmosphere. This has given rise to numerous investigations of SOC because of its sensitivity to changes in land use and management practices. In contrast, the SIC is often assumed to be relatively stable and its

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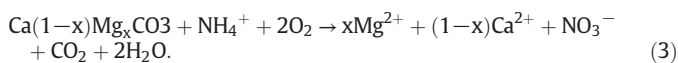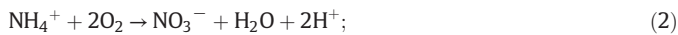
exchange with the atmosphere represents a minor contribution to the terrestrial C balance with an estimated rate of 1.0–5.0 g C m^{-2} yr^{-1}. However, recent study has shown that non-biological processes of carbon absorption could be as high as 62–622 g C m^{-2} yr^{-1} (Xie et al., 2009). Correspondingly, Yang et al. (2012) demonstrated that SIC stocks in the top 10 cm have decreased significantly in Chinese grasslands with a mean rate of 26.8 g C m^{-2} yr^{-1}. Therefore, understanding the role of SIC as a source is crucial for assessing regional, continental, and global soil C stores and predicting the consequences of global change.

Anthropogenic nitrogen (N) enrichment of ecosystems, mainly from fertilizer application and fuel combustion, changes biogeochemical cycling in a way that leads to an altered terrestrial C balance. Numerous studies have examined the effects of nitrogen fertilization on carbon sequestration. N fertilizer is widely perceived to increase SOC by increasing crop residue (organic matter) input to the soil or to decrease SOC by increasing C mineralization (Hyvönen et al., 2008; Pregitzer et al., 2008; Lu et al., 2009; Russell et al., 2009). However, in a few studies, no increase in SOC was observed with N fertilizers, despite the increase in crop residue returned to the soil, due to near the saturation level of organic matter inputs (Brown et al., 2014). Meanwhile, net losses of native SOC that were accelerated by high N fertilization have been found under different cropping systems (Russell et al., 2005; Khan et al., 2007). As for SIC, it has been widely reported to dissolve at increased rates via proton release during nitrification of N fertilizers at the catchment level (Semhi et al., 2000; Barth et al., 2003; Raymond et al., 2008; Barnes and Raymond, 2009; Pierson-Wickmann et al., 2009; Jiang, 2013), potentially leading to direct and indirect CO$_2$ releases to the atmosphere (Perrin et al., 2008). Gandois et al. (2011) found that cation and HCO$_3^-$ leaching increased in carbonate-rich soil after nitrogen fertilizer application in a soil column without crops. However, few studies have reported the direct impact of nitrogen fertilizer on the process of SIC dissolution and release of CO$_2$ in arable land (He et al., 2013).

Generally, the dissolution of carbonate is driven by carbonic acid from the soil or atmospheric CO$_2$ as well as by sulfuric and nitric acids from anthropogenic input. Dissolution of carbonate by carbonic acid from soil/atmospheric CO$_2$ progresses as follows:

$$Ca(1-x)Mg_xCO_3 + H_2O + CO_2 \rightarrow xMg^{2+} + (1-x)Ca^{2+} + 2HCO_3^-. \quad (1)$$

Eq. (1) shows that dissolution of one mole of carbonate requires the uptake of one mole of CO$_2$. This reaction can act as a sink if the HCO$_3^-$ is reacted with external Ca and Mg or is transported into the ocean and utilized by aquatic organisms (Lerman and Mackenzie, 2005; Liu et al., 2010). After spreading ammonium fertilizer, protons are produced during the nitrification process (Eq. (2)). If the carbonic acid in Eq. (1) is replaced with nitric acid produced by those processes, the dissolution of carbonate becomes (Eq. (3)):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+; \quad (2)$$

$$Ca(1-x)Mg_xCO3 + NH_4^+ + 2O_2 \rightarrow xMg^{2+} + (1-x)Ca^{2+} + NO_3^- + CO_2 + 2H_2O. \quad (3)$$

In this reaction, one mole of CO$_2$ will be released as a source. If the soils exhibit higher pH, the CO$_2$ can react continually with carbonate and form HCO$_3^-$. Then, the reaction equation will be as follows:

$$2Ca(1-x)Mg_xCO_3 + NH_4^+ + 2O_2 \rightarrow 2xMg^{2+} + 2(1-x)Ca^{2+} + NO_3^- + 2HCO_3^- + H_2O. \quad (4)$$
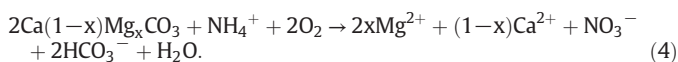
This process is C neutral or a potential C source, until dissolved carbonate reprecipitates and CO$_2$ is released in deeper profiles (Gandois et al., 2011). As the descriptions and equations above, when the equivalent ratio of HCO$_3^-$ / (Ca^{2+} + Mg^{2+}) in soil leachate is above 0.5, the dissolution is driven both by carbon acid and by strong acid, and the CO$_2$ could be taken up from the air. Otherwise, the dissolution is driven only by strong acid and CO$_2$ is released at a ratio below 0.5. In this way, the ratio of HCO$_3^-$ / (Ca^{2+} + Mg^{2+}) in soil leachate can be used to evaluate the driving factors of weathering and the role of carbon sink.

The North China Plain (NCP) is one of China's major agricultural areas (3.3 × 10^5 km^2), providing > 15% of China's total annual grain production and over 19% of its total winter wheat production. Therefore, high levels of nitrogen are commonly applied with an annual average of 500 kg N ha^{-1} for sustaining high yield. Calcareous Fluvo-Aquic is the main soil type in the region, and there is high carbonate content in the topsoil that contains C ranging from 6 to 15 kg C m^{-2} (Wu et al., 2009). It is critical to evaluate the impacts of nitrogen fertilizer on the C behavior and balance, including both organic and inorganic patterns in this specific agricultural area.

In this paper, we studied a wheat-maize double cropping system that received one of four N fertilizer rates (i.e 0–600 kg N ha^{-1} yr^{-1}) for 15 years while all other nutrients were managed for optimum production. The main objectives were: (1) to quantify the effect of N on C sequestration in the topsoil, and (2) to investigate the effect of N on the soil leachate composition as well as the ratio between elements to evaluate the consequences for the CO$_2$ budget.

2. Materials and methods

2.1. Experiment description

The study was conducted at Luancheng Agroecosystem Experimental Station (37°53′ N, 114°41′ E; elevation 50 m) of the Chinese Academy of Sciences. This area is located in the piedmont region of the Taihang Mountains, which are a part of the NCP. Mean annual precipitation is approximately 480 mm, 70% of which falls in July–September. Annual average air temperature is 12.5 °C. The soil type of the area is predominantly calcareous Fluvo-Aquic soil (Argic, Rusty Ustic Cambisols; Zitong, 1999). And the water table is well below the 30 m depth in this area. The basic soil physical and chemical properties are given in Table 1. The predominant cropping system in the region is a winter wheat–corn double-cropping system (Wang et al., 2014). The system is flood irrigated with pumped groundwater three times per year at about 40–60 mm each time, and the details of the water's chemical composition are given in Table S1.

2.2. Field experiment

Field experiments were established in 1998 with randomized complete block N-response plots (10 m × 7 m) with three replicates. The plots were fertilized 4 times per year at four different urea N application rates, viz., no fertilizer input (CK), 200 kg N ha^{-1} yr^{-1} (N$_{200}$), 400 kg N ha^{-1} yr^{-1} (N$_{400}$), and 600 kg N ha^{-1} yr^{-1} (N$_{600}$). In addition, the plots received 65 kg P ha^{-1} yr^{-1} as superphosphate (P$_2$O$_5$: 12%; CaO: 24%). Control of weeds, pests, and disease were conducted according to local practices. After harvest, the wheat and maize residue were mechanically chopped (<5 cm) and incorporated into the soil. The fields were ploughed by rotary cultivator after maize harvest. Wang et al. (2014) provides further details on fertilizer regime.

2.3. Soil sampling and measurement

After corn harvest in 2012, soil cores (0–100 cm deep) from each plot were collected using a soil auger (4 cm in diameter). These cores were divided into sections of 0–20, 20–40, 40–60, 60–80, and 80–100 cm depth. After bulk density was measured, each soil sample was thoroughly sieved to 2 mm. The sieved samples were air-dried for subsequent analysis of chemical properties. Concurrently, soil samples without replicates (1 core per plot and the 3 plots mix together) were collected at the 0–12 m depth in each nitrogen treatment. These

Table. 1
The initial soil physical and chemical characteristics at the long-term experiments site.

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Dry bulk density (g cm^{-3})	CEC (mmol/kg)	Total nitrogen (g N g^{-1})	Total phosphorus (g kg^{-1})	Total potassium (g N kg^{-1})
0–20	12.5	34.2	12.2	1.41	125	1.13	0.76	16.6
20–40	13.3	33.6	13.3	1.60	131	0.82	0.62	16.7
40–60	13.8	31.2	13.7	1.58	158	0.53	0.41	17.0
60–80	15.4	33.2	15.4	1.44	122	0.45	0.35	16.9
80–100	16.0	34.0	16.0	1.44	68	0.60	0.37	16.7

CEC indicates cation exchange capacity

samples were used for analysis of leachate. The sample was collected as sequential soil columns (1.2 m long and 43 mm inner diameter) by using Geoprobe (Geoprobe 54DT, USA). The soil columns were brought to the laboratory and divided into approximately 30 layers (0.4 m per layer, except for several special texture transition layers) according to visually identified soil texture. Soil within the same layer was mixed and immediately extracted via distilled water (the ratio of water and soil is 5:1, shaking for a half hour at 20 °C) for soil leachate analysis. Soil organic carbon (SOC) was measured by the $K_2Cr_2O_7$–H_2SO_4 oxidation method of Walkey and Black (Nelson et al., 1982). The concentration of SIC was measured by manometric collection of CO_2 evolved during an HCl treatment process. Leachate samples were analyzed for anions (Cl^-, SO_4^{2-}, and NO_3^-) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) via ion chromatography (IC) and atomic absorption spectrometry (AAS). Based on the distribution balance of carbonic acid system, HCO_3^- is in dominant abundance and almost no H_2CO_3 remained above pH 8.0, so the dissolved inorganic carbon (DIC) was determined as HCO_3^- using an Elementar liquiTOC analyzer. Soil pH was measured via a pH meter using soil mixed with distilled water (ratio 1:2.5).

2.4. Statistical analyses

One-way analysis of variance (ANOVA) was used to determine the effects of N addition on the C storage in soil. Differences between treatment means were compared using Fisher's LSD method at the 0.05 probability level. All analyses were conducted using SPSS statistical software (ver. 11.0, SPSS, Chicago, IL, USA).

3. Results

3.1. Soil pH

Soil pH in 0–20 cm depth significantly decreased from 8.45 to 8.02 with the increase of N application rates (Fig. 1). At 20–40 cm, soil pH in N_{600} was significantly lower than that in the no fertilizer (CK) and N_{200} treatments. At the 40–60 cm depth, soil pH for the CK treatment was significantly higher than in the three N application treatments. Below the 60 cm depth, the difference was not statistically significant.

3.2. SIC and SOC

In the top soil (0–20 cm), SIC contents of all treatments were the lowest (Fig. 2). The values ranged from 5.3 to 4.4 g kg^{-1} and then slightly increased with soil depth. Statistically, SIC content in CK was significantly higher than in N_{200} and N_{600} at 0–60 cm, and SIC content in CK was higher than N_{400} at 40–60 cm. There was no significant difference in the SIC content among nitrogen applications throughout the whole soil profile, except N_{200} which was significantly lower than N_{400} at 0–20 cm. The total stock of SIC at 0–60 cm depth in CK was significantly higher than in the N applications, but the differences at 0–100 cm were not statistically significant.

In contrast to SIC, SOC contents decreased with soil depth; SOC contents at the surface soil were significantly higher than those in deeper soils (Fig. 2). Statistically, SOC content in CK was significantly lower than in the N applications in each layer, except for N_{200} in 20–40 cm.

The total stock of SOC at both 0–60 cm and 0–100 cm depths were significantly increased with N application rates, except that there was no significant difference between N_{400} and N_{600} (Table 2). However, the total soil carbon (SIC + SOC) stock did not differ among the four treatments in the 0–60 cm or 0–100 cm layer, because the increase of SOC is offset by the decrease of SIC. The C gain/loss efficiency was calculated as the units of C gained or lost in soil pool per units of N added (Table. 2). The C gain efficiency as SOC decreased with increasing nitrogen rates, also the C loss efficiency as SIC decreased with increasing nitrogen rates.

3.3. Soil leachate

Soil leachate chemistry at 0–1200 cm depth was measured via distilled water extraction to investigate the readily leachable cations and anions. The content of HCO_3^- in the 0–80 cm layers increased with N application rates (Fig. 3), while below 400 cm, the content in CK treatments was higher than in the other three treatments. In the 40–440 and 0–160 cm layers, the contents of both Cl^- and SO_4^{2-} in CK were marginally lower than in the other treatments. In addition, the content of SO_4^{2-} in N_{200} was higher than in both the CK and N_{600} at 120–640 cm. The NO_3^- contents in CK and N_{200} was not detected in most layers below 80 cm. However, there was obvious accumulation of NO_3^- in the N_{400} and N_{600} treatments, especially the peaks at depths of 80–440 cm.

As for cations (Fig. 4), the contents of Ca^{2+} and Mg^{2+} in CK was lower than in the other treatments at 120–800 cm depths. The content of K^+ in N_{600} was higher than in the other treatments at 40–80 cm and below 560 cm depth. In contrast, the content of Na^+ in CK was higher than in the N applications for 320–720 cm and below 840 cm depth.
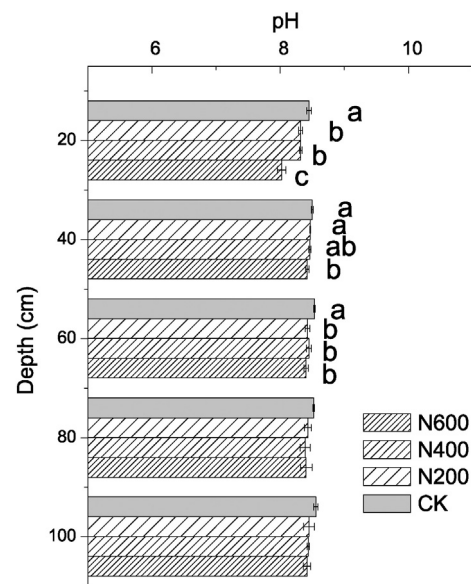

Fig. 1. The distribution of soil pH values in profiles with different rates of N application after 15 years (different letters within the same depth indicate significant difference at $P < 0.05$).
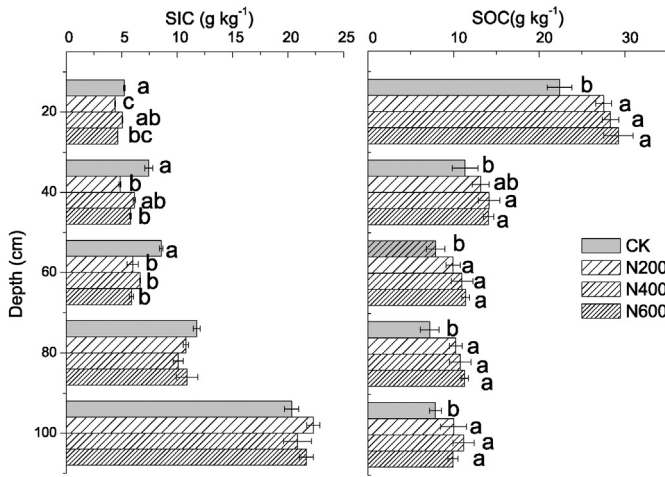
Fig. 2. The distribution of SIC and SOC in profiles with different rates for the 15-years of continuous N application (different letters within the same depth indicate significant difference at $P < 0.05$).

The relationship of Ca^{2+} and Mg^{2+} to carbonate alkalinity in soil leachates can provide some information about the dissolution of SIC by different protons from strong acid or carbonic acid. For all the treatments, the distribution of the charge equivalent ratios of Ca^{2+} and Mg^{2+} to HCO_3^- varied from 3.3 to 0.30. This higher ratio in upper layers under nitrogen application indicates that carbonic acid is probably an important weathering agent besides protons from nitrification in the area. The ratio in 0–80 cm layers increased with N application rates, while the ratio in CK treatments was higher than in the other three treatments below 120 cm depth.

4. Discussion

4.1. SOC and SIC

The soil organic carbon stock increased in the topsoil (0–20 cm) after the 15 years of continuous N applications, which is consistent with other findings in the North China Plain (Cai and Qin, 2006; Zhang et al., 2010) and other areas around the world (Hyvönen et al., 2008; Pregitzer et al., 2008; Lu et al., 2009; Russell et al., 2009). The increase of SOC under N application may be associated with higher organic carbon input and/or lower rates of SOC decomposition. It has been reported that increasing the amount of N from 400 to 600 has no significant effect on crop biomass, similar to the SOC storage trends in this experimental field (Qin et al., 2012). This suggests that the input of crop residues and roots were the main contributors to the change of stored SOC. Moreover, in this study the soil C/N ratio increased with N application rates below 20 cm (Fig. S1), indicating that the decomposition of SOC decreased in deeper soil. This result is consistent with a meta-analysis which concluded that N fertilization decreased soil C turnover rate or increased residence time in agricultural systems, as microbial activities

may be repressed by N addition in low C:N ratio soil (<15, in most agricultural soils) (Lu et al., 2011).

The soil also accumulated more SOC in the subsoil (60–100 cm) during the 15 years of continuous N treatments than the CK (Fig.2). >64% of the total SOC accumulation occurred in the subsoil (20–100 cm) for all treatments, and deeper SOC may be more stable because the subsoil environment does not unfavorable to the mineralization of soil C (Liu et al., 2003; Harrison et al., 2011). Thus, both the subsoil and the topsoil under nitrogen application need to be considered when reevaluating carbon sequestration.

The SIC stocks at 0–60 cm depth decreased by 13.6–18.6 Mg ha^{-1} after 15 years of nitrogen application, with an average rate of 91–124 g C m^{-2} yr^{-1}. This result is consistent with reports that SIC decreased by 230.8 to 623.9 g C m^{-2} in the 0–100 cm soil layer after 6 years of N addition in Inner Mongolian grasslands (He et al., 2013). The decrease in SIC may be the result of protons released from nitrification of nitrogen fertilizer, followed by decreases in the soil pH. Studies have also shown that column experiment N additions (e.g., fertilizers and manure) aid in the dissolution of carbonate and increase the total export of dissolved inorganic C (DIC) at the catchment level (Barnes and Raymond, 2009).

4.2. Driving force of dissolution of carbonate and the effect on CO_2 uptake

Theoretically, 1 kg N of ammonium fertilizer can produce 0.19 k mol acid (+) and dissolve a maximum of 1.7 kg of C soil carbonate, as in Eq. (4). However, the loss efficiency of SIC in this study is higher or equal to this value for the N$_{200}$ (6.2), N$_{400}$ (2.3), and N$_{600}$ (1.6) treatments. This result was obtained even though all the protons could not have fully reacted with carbonate and the nitrification was incomplete (uptake in ammonium form by crop and ammonia emission). The input of Ca and Mg from the irrigation or fertilizer may impact the soil carbonate. The soluble Ca^{2+} in superphosphate can produce a maximum of 1.04 Mg ha^{-1} carbon as carbonate after 15 years of superphosphate use, which is much less than the change in carbonate in soil after nitrogen treatments. Similarly, irrigation can cause the formation of a maximum of about 1.5–2.0 Mg ha^{-1} carbon. Due to similar management at field, the effect of irrigation and application superphosphate on the difference of carbonate among treatments is negligible in this study. These analyses indicate that other processes beside nitrification must also be driving the decrease in carbonate content in the 0–60 cm soil layers.

Neither sulfides nor sulfur as fertilizer was applied during this experiment or before it began, so little sulfuric acid was produced from the oxidation of those reduced sulfurs. The sulfuric input from deposition or other process were the same as in the control (no fertilizer), they cannot account for the dissolution of carbonate in N application treatments. On the other hand, higher CO_2 partial pressures associated with respiration are derived from soil organic matter or higher carbon input from aboveground and belowground litter, which favor dissolution of carbonate (Kuzyakov et al., 2006).Thus, we suspect that the increased loss of carbonate at lower nitrogen applications derives from dissolution by carbonic acid. Our other findings support this interpretation, as there are negative relationships between SIC and SOC across all the

Table 2
The change of carbon storage and C loss/gain efficiency with 15 years of continuous N application at different rates.

	SIC storage (Mg ha^{-1})		SOC storage (Mg ha^{-1})		TC storage (Mg ha^{-1})		C loss/gain efficiency in 0–60 cm (g C g^{-1} N added)		
	0–60 cm	0–100 cm	0–60 cm	0–100 cm	0–60 cm	0–100 cm	SIC	SOC	TC
CK	66.0a	138.8	53.8c	61.6c	119.8	200.4	–	–	–
N200	47.4b	125.8	65.5b	76.9b	112.9	202.7	6.2	3.4	−2.3*
N400	52.3b	124.5	69.1a	81.8a	121.4	208.9	2.3	2.6	0.3
N600	50.8b	127.2	70.7a	82.4a	121.5	209.6	1.6	1.9	0.2

Different letters in the same column indicate a significant difference at $P < 0.05$. SIC indicates soil inorganic carbon, SOC indicates soil organic carbon, and TC represents total carbon. C loss/gain efficiency can be calculated as the units of C gained or lost in soil pool per units of N added. The negative value labeled by "*" represents the lost carbon.
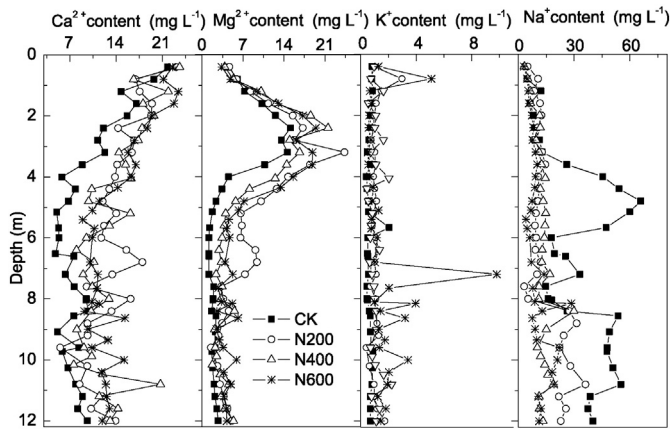
Fig. 3. Profile distribution of soil leachate cation concentration with different rates for the 15 years of continuous N application.

treatments (Table S2). Moreover, it was found that the amount of HCO_3^- and the $HCO_3^- / (Ca^{2+} + Mg^{2+})$ ratio (above 0.5) in soil leachate at the 0–80 cm depth were higher in N application treatments than in the CK (Fig.4 and Fig.5). This also suggests that dissolution of carbonate increased and was mainly driven by soil carbonic acid as well as by protons directly through the nitrification (Hamilton et al., 2007).

The reprecipitation of dissolved carbonate in the lower soil profile and in river systems also impacts the strength of carbonate as a C sink or source. In our study, both the amount of HCO_3^- and the $HCO_3^- / (Ca^{2+} + Mg^{2+})$ ratio in soil leachate for N application treatments were lower than those in the CK below the 320 cm depth(Fig.4 and Fig.5). It appears that the dissolved carbonate reprecipitated above this layer and the CO_2 absorbed by carbon dissolution was released into the atmosphere again. However, it was found that the SO_4^{2-} concentration increased in N application treatments in most layers (Fig. 5), although the increase could not be explained by the input of sulfuric or oxidation of reduced sulfur as described above. Limited downward leaching can result in significant accumulation of sulfate in subsurface horizons, which is a common phenomenon in soil under semiarid conditions, especially with restricted drainage. Because sulfate's most common form is a cocrystallized impurity in calcium carbonate, it is only be released by carbonate mineral dissolution(Bettany et al., 1982; Schoenau and Malhi, 2008). The increase in SO_4^{2-} concentration might have been caused by dissolution of the sulfate-$CaCO_3$ that co-precipitate in upper layers of soil via carbonic acid or protons from nitrification (Hu et al., 2005). This is also similar to findings from one column experiments where liming increased SO_4^{2-} concentration in wheat fields (Ahmad et al., 2013). This weathering process of the
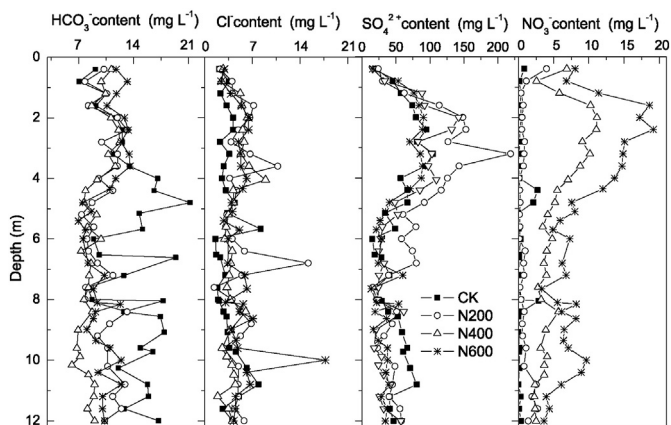
compound was found to release Ca^{2+} and/or Mg^{2+} without producing equivalent carbonate ions. This is another reason for the decrease in the $HCO_3^- / (Ca^{2+} + Mg^{2+})$ ratio besides the reprecipitated carbonate. Furthermore, the dissolved calcium sulfate can precipitate HCO_3^- at deeper layers with higher pH as a C sink, but this process does not release CO_2 (Renforth et al., 2012). In addition, we found that the Na^+ and pH in the CK below 320 cm depth were much higher than those in the N application treatments, showing that the soil exhibits high chemical dispersion associated with Na^+ alkalinity and the infiltration may also be hindered in deeper layers (Qadir et al., 2001). Thus, it is possible that HCO_3^- and other anions in the nitrogen treatments more easily infiltrated into deeper layers compared to the CK. This can be viewed as a CO_2 sink considering the combined action of carbonate dissolution, the global water cycle, and photosynthetic uptake of DIC by aquatic organisms.

4.3. Reevaluation of CO_2 budget with nitrogen application

Although the quantification of reprecipitation and direct CO_2 release from dissolution of carbonate cannot be determined based on our experiments, we can assess the range of the CO_2 sink strength in soil with certain rates of nitrogen application based on the above three equations (Eqs. (1) (3) and (4)). If we assume that dissolved carbonate is retained fully in soil and not reprecipitated, the maximum CO_2 sink is induced as in Table 3. If we assume the opposite, CO_2 is released and the minimum CO_2 sink is induced.

For the scenario of minimum CO_2 sequestration, the carbonate released as CO_2 represent 36% to 57% of the total carbonate lost in the three nitrogen application rates. However, this was partly offset by the increase of SOC. The scenario of minimum CO_2 sequestration usually occurs at low pH (below 6.3), but this may be unlikely in this study due to the higher pH in deeper profiles (above 8.43). For the scenario of maximum CO_2 sequestration, the dissolution of carbonate at low nitrogen
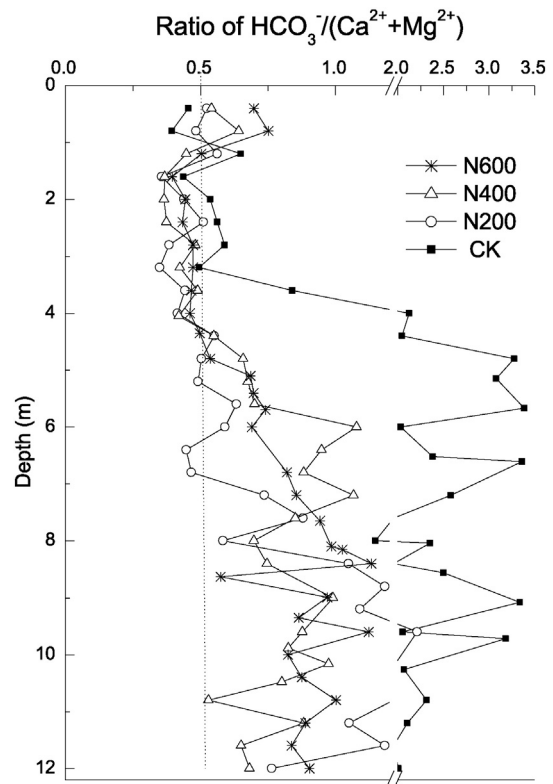

Fig. 4. Profile distribution of soil leachate anion concentration with different rates for the 15 years of continuous N application.

Fig. 5. Profile distribution of charge equivalent ratio of $HCO_3^- / (Ca^{2+} + Mg^{2+})$ in soil leachate with different N application after 15 years. The theoretical line at 0.5 (corresponding to expected $HCO_3^- / (Ca^{2+} + Mg^{2+})$ ratio according to Eq. (4)) is indicated.

Table 3
A budget for CO_2 sinks after applying nitrogen at different rates in calcareous soil.

	CK	N_{200} (Mg ha^{-1})	N_{400} (Mg ha^{-1})	N_{600} (Mg ha^{-1})
ΔSOC in 0–100 cm (1)	–	15.3	20.2	20.8
ΔSIC in 0–60 cm (2)	–	−18.6	−13.6	−15.2
Theory dissolution by nitrification (3)	–	−2.6	−5.1	−7.7
Min CO_2 sinks (1) + (3)	–	12.7	15.1	13.1
Max CO_2 sinks (1) − [(2) − (3) ∗ 2)]	–	28.7	23.7	20.6

ΔSOC indicates the difference of soil organic carbon between the treatments with nitrogen application and the control treatment (CK); ΔSIC indicates the difference of soil inorganic carbon between the treatments with nitrogen application and the control treatment (CK).

levels (the N_{200} and N_{400} treatments) acted as a CO_2 sink and increased the SOC. However, CO_2 was released for higher nitrogen levels. This may be due to the lower pH and the dissolved carbonate not being fully retained in soil solution.

Our results show that the CO_2 sink strength is intermediate to the two extreme assumptions of Table 3, but at lower level of nitrogen treatment, the dissolution of carbonate is was more likely to sequester CO_2 than to act as a net source. Thus, at lower nitrogen application levels, the CO_2 sequestration based on the exchange of total carbon in the upper layers may be underestimated (Table 2). To accurately evaluate soil C sequestration under N input scenarios in semi-arid regions, one must consider changes of SIC storages as well as the fractions of dissolution with different sources of acids and precipitation in soil profiles. Our study just is the stoichiometric analysis of carbonate weathering process and driving factors. There may be other strong acids entered into the system or formed in the soil impacting the process. This must to be verified by the advanced measurement of CO_2 flux method in future studies.

5. Conclusion

We examined the changes in the SOC and SIC stocks of the topsoil and subsoil following the long-term nitrogen application in North China Plain. After 15 years, nitrogen application in calcareous soil can significantly increase the SOC pool not only in the top 0–30 cm but also in the subsoil (30–100 cm). In contrast, nitrogen application decreased the SIC accumulation in the 0–60 profiles. The measured loss of carbonate was much higher than the theoretical values of dissolution at maximum by protons from nitrification after applied nitrogen. Furthermore, the amount of HCO_3^- and the $HCO_3^- / (Ca^{2+} + Mg^{2+})$ ratio in soil leachate were higher in N application plots than those in the CK in 0-80 cm depth in soil profile. Therefore, we speculate that the dissolution of carbonate is driven by carbonic acid from soil or atmosphere CO_2, as well as by protons from nitrification after N applied. Due to easier infiltration and more external Ca^{2+} and Mg^{2+} from dissolved calcium sulfate, dissolution of carbonate is more likely to sequester CO_2 than to act as a net source at lower nitrogen applied. Therefore, it might be underestimated the CO_2 sink based on the exchange of total carbon in the upper layers. To accurately evaluate soil C sequestration under N input scenarios in semi-arid regions, future studies should not only include changed of SIC storages, but also the fractions of dissolution with different source of acids and precipitation in soil profiles.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.04.115.

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