# Effect of amending nitrogen on the total carbon of arable soil in semi-arid region

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## 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 at the field level. This study determined the soil organic/inorganic carbon storage in the soil profile at 0–100 cm depths in 4 N application treatments (0, 200, 400, and 600 kg N ha$^{-1}$ y$^{-1}$) for 15 years in the North China Plain. 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$_2$.

## Key Words

Carbon storage, Nitrogen, Arable soil, Semi-arid region

## Introduction

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. 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, 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 (, 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  potentially leading to direct and indirect CO$_2$ releases to the atmosphere(Semhi *et al.*, 2000, Pierson-Wickmann *et al.*, 2009, Jiang, 2013),. 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.

The North China Plain (NCP) is one of China's major agricultural areas ($3.3 \times 10^5$ km$^2$), providing more than 15% of China's total annual grain 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.

## Methods

### Experiment description

The study was conducted at Luancheng Agroecosystem Experimental Station 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. The system is flood irrigated with pumped groundwater three times per year at about 40-60 mm each time.

### 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.

*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. The samples were air-dried for analysis of chemical properties. Concurrently, soil samples without replicates were collected at the 0-12 m depth in each nitrogen treatment. These 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 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 for soil leachate analysis. Soil organic carbon (SOC) was measured by the $K_2Cr_2O_7$–$H_2SO_4$ oxidation method. 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.

*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).

**Results**

*SIC and SOC*

In the top soil (0-20 cm), SIC contents of all treatments were the lowest (Fig. 1). 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. 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 0-100 cm depths was significantly increased with N application rates, except that there was no significant difference between $N_{400}$ and $N_{600}$ (Tab.1). 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. The C gain/loss efficiency was calculated as the units of C gained or lost in soil pool per units of N added (Table. 1). The C gain efficiency as SOC decreased with increasing nitrogen rates, also the C loss efficiency as SIC decreased with increasing nitrogen rates.

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 & Qin, 2006). 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.

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 & Raymond, 2009). 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. 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). 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. 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.

*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, while below 400 cm, the content in CK treatments was higher than in the other three treatments. As for cations, the content of $Ca^{2+}$ and $Mg^{2+}$ in CK was lower than in the other treatments at 120-800 cm depths. 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 (Fig. 2). 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.

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.2). 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 (date not shown), 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(Schoenau & 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). 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
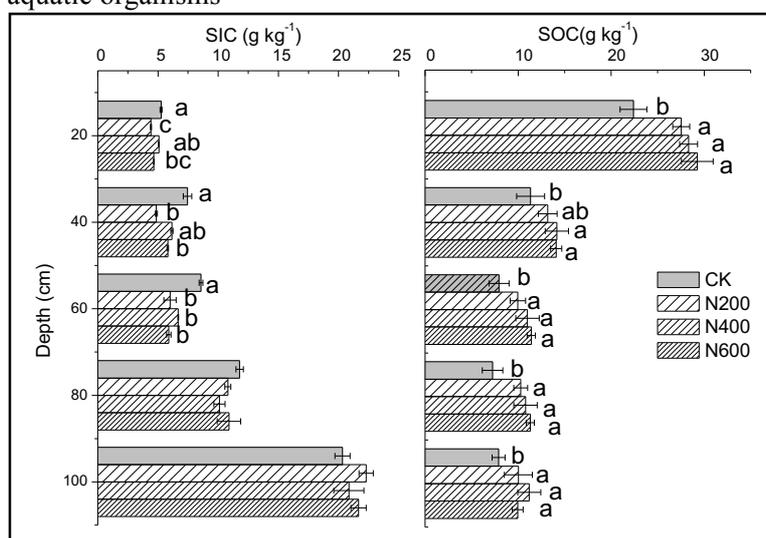


Fig. 1 The distribution of SIC and SOC in profiles with different rates for the 15-years of continuous N application (different letters within the same depth indicate significant difference at P < 0.05)

Table 1 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 0-60cm (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 |

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.
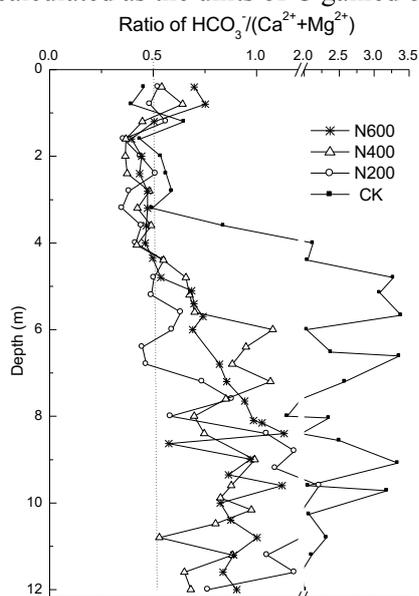


Fig. 2 Profile distribution of charge equivalent ratio of $HCO_3^-/(Ca^{2+} + Mg^{2+})$ in soil leachate with different N application after 15 years.

## 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 in the top 0-100 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 0-80cm 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. 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.

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