PRIMARY RESEARCH ARTICLE

Global Change Biology WILEY

Dramatic loss of inorganic carbon by nitrogen-induced soil acidification in Chinese croplands

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Funding information
National Natural Science Foundation of China (41671295), National Key R & D Program of China (2017YFD0200106), 111 Project (B12007)

Abstract

Intensive crop production systems worldwide, particularly in China, rely heavily on nitrogen (N) fertilization, but left more than 50% of fertilizer N in the environment. Nitrogen (over) fertilization and atmospheric N deposition induce soil acidification, which is neutralized by soil inorganic carbon (SIC; carbonates), and carbon dioxide (CO_2) is released to the atmosphere. For the first time, the loss of SIC stocks in response to N-induced soil acidification was estimated for Chinese croplands from 1980 to 2020 and forecasts were made up to 2100. The SIC stocks in croplands in 1980 were 2.16 Pg C (16.3 Mg C/ha) in the upper 40 cm, 7% (0.15 Pg C; 1.1 Mg C/ha) of which were lost from 1980 to 2020. During these 40 years, 7 million ha of cropland has become carbonate free. Another 37% of the SIC stocks may be lost up to 2100 in China, leaving 30 million ha of cropland (37.8%) without carbonates if N fertilization follows the business-as-usual (BAU) scenario. Compared to the BAU scenario, the reduction in N input by 15%–30% after 2020 (scenarios S1 and S2) will decrease carbonate dissolution by 18%–41%. If N input remains constant as noted in 2020 (S3) or decreases by 1% annually (S4), a reduction of up to 52%–67% in carbonate dissolution is expected compared to the BAU scenario. The presence of $CaCO_3$ in the soil is important for various processes including acidity buffering, aggregate formation and stabilization, organic matter stabilization, microbial and enzyme activities, nutrient cycling and availability, and water permeability and plant productivity. Therefore, optimizing N fertilization and improving N-use efficiency are important for decreasing SIC losses from acidification. N application should be strictly calculated based on crop demand, and any overfertilization should be avoided to prevent environmental problems and soil fertility decline associated with $CaCO_3$ losses.

KEYWORDS
carbon sequestration, carbonate dissolution, CO_2 efflux, pedogenic carbonates, soil acidification, soil inorganic carbon

1 | INTRODUCTION

There are two carbon (C) pools in the soil, that is, soil organic C (SOC) and soil inorganic C (SIC). To mitigate the increasing levels of

carbon dioxide (CO_2) in the atmosphere, almost all previous studies are devoted to SOC because it is associated with and reflects various ecosystem functions, as well as responds quickly to land-use changes and agricultural management practices such as tillage and fertilization (Lal, 2004; Sanderman, 2012; Sheng et al., 2015; Yan et al., 2012). Compared to the short turnover rate of SOC (a few years to centuries), SIC has a considerably longer turnover rate


Sajjad Raza and Miao Na have contributed equally to this work. See Letter to the Editor on this article by Guo and Chen, 27, 957–958 and the response to the letter on this article by Raza et al., 27, e7–e10.

(~85,000 years; Schlesinger, 1985; Zang et al., 2018). Therefore, its role in mitigating CO_2 efflux is usually neglected. However, recent studies have reported that CO_2 absorption occurs in alkaline soils and deserts by abiotic mechanisms (Li, Wang, Houghton, & Tang, 2015; Wang, Wang, et al., 2015; Xie, Li, Zhai, Li, & Lan, 2009; Zhao, Zhao, Wang, Stahr, & Kuzyakov, 2016). Agricultural practices can also fundamentally alter the SIC cycle (Lal & Kimble, 2000; Raza et al., 2019; Rey, 2015). The contribution of SIC to CO_2 efflux should not be neglected and SIC maintenance has great significance for decreasing C losses and maintaining soil health and productivity (Zamanian & Kuzyakov, 2019; Zamanian, Zarebanadkouki, & Kuzyakov, 2018).

In arid, semiarid and subhumid regions, SIC comprises more C than SOC (Lal, 2008). The total stock of SIC at the global level ranges from 695 to 1,738 Pg (1 Pg = 10^{15} g) in the upper 100 cm (Batjes, 1996; Eswaran, Berg, Reich, & Kimble, 1995). The total SIC storage is 50–60 Pg C in China, which is mainly located in arid and semiarid regions in the northwest (approximately 47% of the total land surface; Mi et al., 2008; Wu, Guo, Gao, & Peng, 2009).

SIC stability is largely dependent on soil pH. Soil acidification is driven by several processes (Figure 1): (a) nitrification of NH_4^+ added as fertilizers, atmospheric N deposition, biological N_2 fixation (legumes and bacteria), and mineralization of soil organic matter (SOM; Equation 1); (b) H^+ release by roots for cation/anion balance by nutrient uptake; (c) acid deposition; (d) removal of base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) by leaching; (e) dissolution of CO_2 released from roots and microbial respiration as well as from SOM mineralization, followed by subsequent protonation; and (f) release of organic acids during SOM mineralization, by roots into the rhizosphere and by microbial metabolic activity (Bolan, Curtin, & Adriano, 2005; Goulding, 2016; Kuzyakov & Razavi, 2019):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+. \tag{1}$$
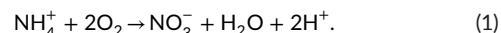
Soils buffer the acidity by the following mechanisms (Figure 2): (a) dissolution of sodium carbonates (Na_2CO_3) in alkaline soils; (b) dissolution of calcium and magnesium carbonates ($CaCO_3$, $MgCO_3$) in saline soils; (c) weathering of silicate minerals; (d) exchange of H^+ with base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) in clay minerals and organic matter; (e) dissociation of aluminum (Al)-hydroxyl complexes; and (f) dissociation of iron (Fe) from Fe–hydroxyl complexes (Cai et al., 2015; De Vries, Posch, & Kämäri, 1989; Ulrich, 1986).

In soils with pH > 6.5, carbonates are the main and first buffering system (Bloom, Skyllberg, & Sumner, 2005; Huang et al.,
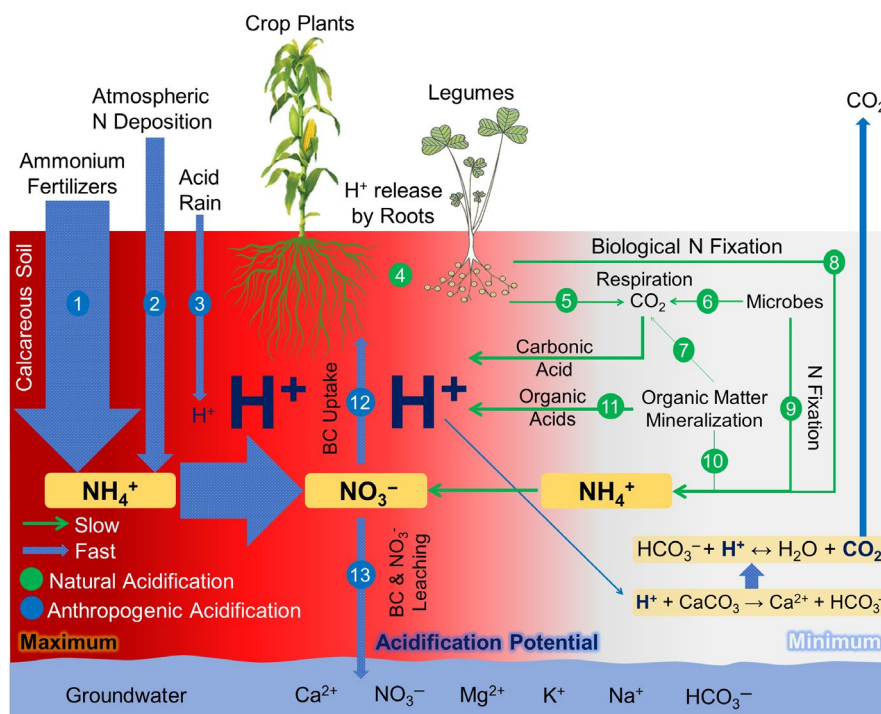

FIGURE 1 Main sources of N input into the soil and related acidification processes leading to CaCO3 dissolution: (1) nitrification of NH_4^+ fertilizers; (2) nitrification of NH_4^+ coming by wet and dry atmospheric N deposition; (3) acid rain; (4) H^+ release by roots for cation/anion balance; (5–7) dissolution of CO_2 from root and microbial respiration, and organic matter and plant residues mineralization, and subsequent H_2O dissociation; (8–10) nitrification of NH_4^+ coming from N_2 fixation by legumes and microbes as well as from soil organic matter (SOM) mineralization; (11) release of organic acids during SOM mineralization; (12, 13) H^+ release in response to base cations (BC) uptake by plants and its removal from soil as leaching. The intensity of the red color shows the soil acidification potential of various processes. The width of the arrows is roughly proportional to the acidification rate of each process. Natural and anthropogenic sources of soil acidification are presented as green and blue points, respectively. Slow processes are shown as green arrows and fast processes are shown as blue arrows [Colour figure can be viewed at wileyonlinelibrary.com]
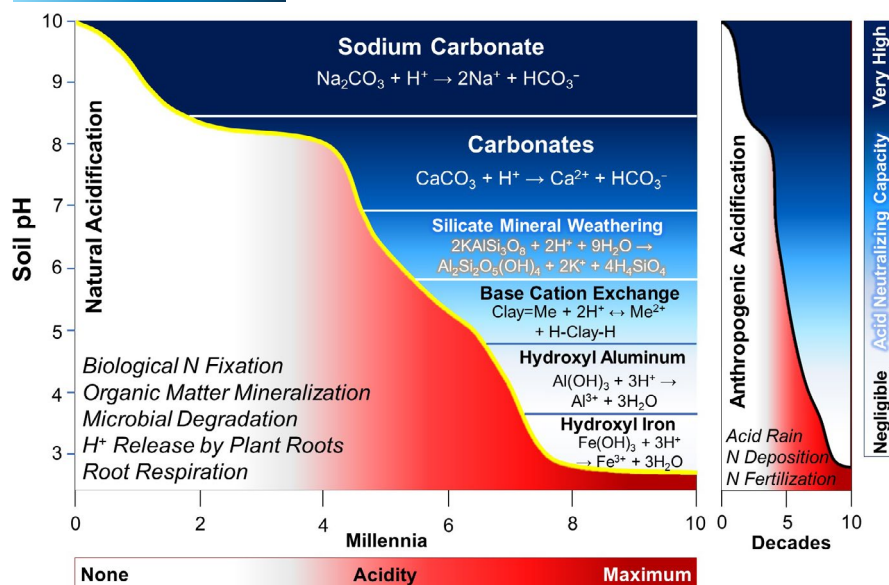
FIGURE 2 Soil buffering systems neutralizing increasing acidity and associated changes in soil pH (left *y*-axis) and their progress under natural (left) and anthropogenic acidification (right). The text in italics on the left-bottom corner shows the main natural and anthropogenic acidification processes (for more processes and details see Figure 1). The yellow curve on the left and black curve on the right show changes in the soil buffering systems with time (millennia for natural and decades for anthropogenic acidification). The blue area above the yellow and black curves shows various soil buffering systems and changes in their acidneutralizing capacity. The red area below the curves shows the changes in soil acidity depending on the buffering systems. The main chemical equations show the respective processes, by which buffering systems neutralize H^+. Me are metal ions such as Ca^{2+} and Mg^{2+} in cation exchange positions. The much smaller area of the right part reflects the much faster (decades) ongoing soil acidification under anthropogenically induced processes, for example, mainly N fertilization–induced acidification. Note that the presented time-line only provides an estimation of the acidification rates, which strongly depend on the pool size of each buffering system and climate condition as well as intensity of N fertilization [Colour figure can be viewed at wileyonlinelibrary.com]

2015). Acidity is neutralized by the acceleration of $CaCO_3$ dissolution (Equation 2; Sanderman, 2012). The dissolution of $CaCO_3$ by acidification leads to CO_2 efflux (Equation 3; Chen, Wang, Luo, & Ye, 2013; Zamanian et al., 2018). Therefore, N fertilization changes the SIC stocks, increases CO_2 efflux to the atmosphere, and subsequently affects the global C cycle and global warming (Dalal, Harms, Krull, & Wang, 2005; Drever & Stillings, 1997; Huang et al., 2015). This is the direct effect of N fertilization on CO_2 release from SIC (Figure 1):

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-, \qquad (2)$$

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O. \qquad (3)$$
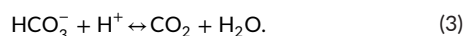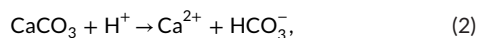
CaCO$_3$ dissolution has several consequences on soil chemistry, physics, micro(biology), and productivity. It decreases soil buffering capacity and results in the leaching of base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+; Lucas et al., 2011). $CaCO_3$ loss decreases the stability of soil aggregates and results in poor structure, aeration, and water permeability of the soil (Fernández-Ugalde et al., 2014). Decreases in soil pH because of $CaCO_3$ loss affect the availability of nutrients, microbial activity, and community structure (Rousk et al., 2010). Therefore, the presence of $CaCO_3$ in the soil is vital for ensuring a favorable environment for plant growth and microbial functions. Consequently, N fertilization-induced soil acidification is crucial

not only for SIC stocks but also for soil fertility and ecosystem functions.

A recent study at the global scale showed that N fertilization-induced H^+ release accelerated $CaCO_3$ dissolution and released a substantial CO_2 amount from the soil (7.48 Tg C/year; Zamanian et al., 2018). In this previous study, H^+ release was calculated based on the total N fertilizer input in the form of urea ($CO(NH_2)_2$). Urea, however, only contributes 48% of the total N fertilizer input worldwide (IFASTAT, 2020). N deposition and losses via ammonia (NH_3) volatilization were considered to be negligible. However, these effects are significant in some parts of the world, especially in soils with high pH, such as in northwest China. The distribution of $CaCO_3$ was obtained from a SIC map, which according to the authors could be a main source of uncertainty in their study (Zamanian et al., 2018). All these factors add to the uncertainty of the estimated results at the global level.

By comparing the differences in SIC stocks from non-cultivated and cultivated lands in China measured during the second national soil survey conducted in the 1980s, Wu et al. (2009) reported that approximately 51% of the cultivated soils had experienced a total SIC loss of 1.6 Pg C due to agricultural land-use activities, including the application of acidifying fertilizers. Since the early 1980s, Chinese agriculture has intensified greatly on a limited land area with large inputs of mineral fertilizers (especially N), which has led to greatly increased crop production. The average N fertilizer input in China

during 2011–2017 was 240 kg N ha^{-1} year^{-1}, which was much higher than the average N input of 75 kg N ha^{-1} year^{-1} in developed countries (FAOSTAT, 2020). The N fertilization in highly intensive cultivation systems (e.g., orchards and greenhouse vegetables) can be as high as 500 kg N ha^{-1} year^{-1} or greater (Lu et al., 2016). Decreasing nitrogen-use efficiency (NUE) by crops means that the majority of the applied N is lost to the environment and adjacent ecosystems, causing negative effects (Guo et al., 2010; Yan et al., 2014; Zhang et al., 2015). The atmospheric N deposition has increased concurrently with N fertilization from 4.6 kg N ha^{-1} year^{-1} in 1981 to 23.2 kg N ha^{-1} year^{-1} in 2010 and contributes substantially to total N input on Chinese croplands (Gu, Ju, Chang, Ge, & Vitousek, 2015; Liu et al., 2013).

Soil acidification driven by nitrification is at least 10–100 times greater than acid deposition in China (Guo et al., 2010). Some studies have highlighted the increasing threat of acidification induced by N fertilization over the past decade (Guo et al., 2010; Zhou et al., 2014; Zhu et al., 2020). Soil acidification rate has increased from 2.6 to 7.6 keq H$^+$ ha^{-1} year^{-1} in the past 30 years in China (Zhu et al., 2018). Major cropland soils were acidified (0.13–0.80 pH units) during the 1980s–2000s mainly due to high amounts of N fertilization (Guo et al., 2010). Grasslands in China have lost SIC at a mean rate of 268 kg C ha^{-1} year^{-1}, mainly due to acidification induced by atmospheric N deposition, N uptake by plants, and SOM mineralization (Yang et al., 2012). Compared to grasslands, N fertilization is very high in croplands. However, the consequences of soil acidification on CaCO$_3$ dissolution and CO$_2$ emissions from Chinese croplands are rarely acknowledged.

The objectives of the present study were to: (a) quantify the changes in CaCO$_3$ stocks due to N fertilization-induced soil acidification, (b) estimate the amounts of CO$_2$ released because of N fertilization-induced CaCO$_3$ dissolution, and (c) predict the areas that are at risk of depleting CaCO$_3$ and more vulnerable to the adverse effects of acidification up to 2100.

2 | MATERIALS AND METHODS

2.1 | SIC stocks

The SIC stocks in croplands of each province in China in 1980 were calculated based on the 34,411 soil profile samples taken during the second national soil survey (NSSO, 1994). Data regarding CaCO$_3$ contents, soil pH, bulk density, percentage of rock fragments (>2 mm), and other parameters were available from various depths for each profile and province based on various soil types (i.e., groups and subgroups; NSSO, 1994). Soil types that were not under agricultural use were excluded from the study. In this meta-analysis, we only focused on the SIC stock in the area under crop cultivation in the upper 0–40 cm soil layer because nitrification is particularly fast in the topsoil (Ghimire, Machado, & Bista, 2017). N fertilization is relevant only for the Ap horizon and most (>95%) N uptake by roots occurs in the upper 40 cm.

SIC stock was calculated using the following equation (Wu et al., 2009):

$$SIC - C = \sum_{i=1}^{n} 0.12 \times d_i \times \rho b_i \times \frac{IC_i}{100} \times \left(1 - \frac{rf_i}{100}\right) \div 10, \quad (4)$$

where n is the number of horizons; d_i, ρb_i, IC_i, and rf_i represent depth (cm), bulk density (g/cm^3), inorganic C content (%) mainly as CaCO$_3$, and % of rock fragments (>2 mm), respectively; and i is the soil layer.

2.2 | Amount and forms of N fertilization and deposition

Legumes fix atmospheric N$_2$ to NH$_4^+$ (biological N fixation; BNF), which causes soil acidification after it progresses through the nitrification process (Figure 1). However, continuous decreases in yield and planting area of legumes indicate that the contribution of BNF to total N input (~4%) and associated acidification is minimal in China (He et al., 2018; Wang et al., 2014). Thus, N fertilization and atmospheric N deposition are the major N sources contributing to accelerated soil acidification (Guo et al., 2010; Liu et al., 2013). Therefore, we only quantified the acidification effects that were induced by nitrification of NH$_4^+$ input via N fertilization and deposition on changes in CaCO$_3$ dissolution and CO$_2$ release from Chinese croplands during the last four decades (1980–2020) and made predictions up to 2100.

The N fertilizer input for each province from 1980 to 2016 was collected from the National Bureau of Statistics of China (NBSC, 2018). The annual N deposition in each province from 1980 to 2010 was obtained from Liu et al. (2013). Bulk N deposition (wet and dry) is dominated by NO$_3^-$ and NH$_4^+$ in China. Because NO$_3^-$ does not undergo nitrification, only the NH$_4^+$ input from deposition was considered as relevant for acidification. The amount of NO$_3^-$ deposition was subtracted from the bulk N deposition using the NH$_4^+$/NO$_3^-$ ratio (Liu et al., 2013). N fertilization and deposition were extrapolated with a 1% annual increase to obtain the N input up to 2100 (Zhu et al., 2020; Table S1).

A total of 11 types of N fertilizers are used in China, five of which comprise up to 98% of the total N fertilization (Figure 3). Each type of N fertilizer source has specific potential to cause soil acidification given the differences in N forms and amount of H$^+$ released (Table 1). During 1980–1996, ammonium bicarbonate (NH$_4$HCO$_3$) and urea (CO(NH$_2$)$_2$) were the two major N fertilizer types, comprising >90% of the total N fertilizer consumption in China. However, the use of NH$_4$HCO$_3$ has decreased with time and has been replaced by NPK compound fertilizers (Figure 3). The types of N fertilizers that were used during 1980–2016 were obtained from IFASTAT (2020) and the same ratio of these types of N fertilizers was used to calculate the contribution of each fertilizer type to total N consumption in each province.

N losses via NH$_3$ volatilization are significant in China (Kang et al., 2016), especially in calcareous soils with pH > 7.0. Therefore,
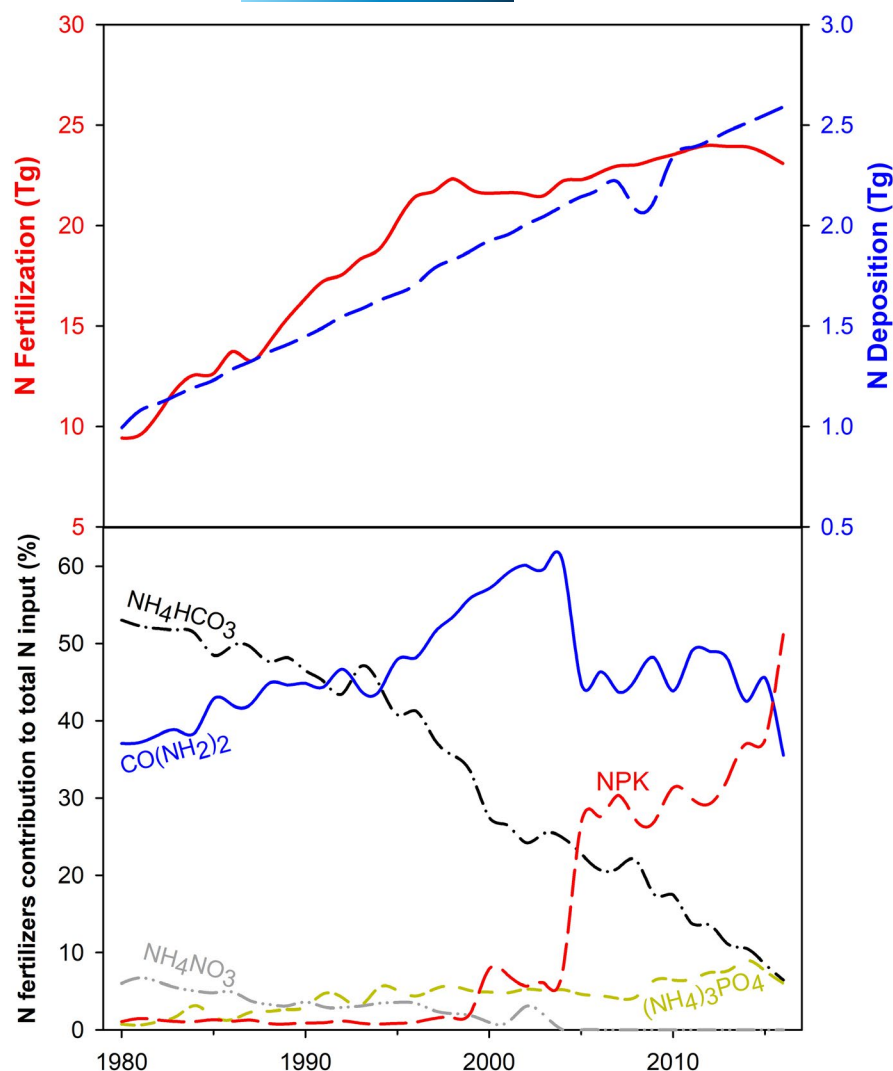
FIGURE 3 Total N inputs from fertilizers and atmospheric deposition (top) and contribution of the five most common N fertilizers (98% of all N fertilizers) in Chinese croplands during 1980–2016 (IFASTAT, 2020; bottom). The following fertilizers were used: $CO(NH_2)_2$ is urea, NH_4HCO_3 is ammonium bicarbonate (ammonium hydrogen carbonate), NH_4NO_3 is ammonium nitrate (ammonium salpeter), $(NH_4)_3PO_4$ is ammonium phosphate, and NPK is compound fertilizer. The decrease in total N deposition in Chinese croplands during 2008–2009 was due to decreases in the total cropland area [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Direct potential of N fertilizer types and N deposition on proton (H^+) release and indirect effects on $CaCO_3$ dissolution and CO_2 efflux from soil

N source	N contents (%)	Chemical reaction in soil	H^+ release (mol)	$CaCO_3$ dissolution (mol)	CO_2 emission (g)
$CO(NH_2)_2$	46	$CO(NH_2)_2 + 4O_2 \rightarrow 2NO_3^- + H_2O + 2H^+ + CO_2$	2	1	12
NH_4NO_3	35	$NH_4NO_3 + 2O_2 \rightarrow 2NO_3^- + H_2O + 2H^+$	2	1	12
NH_4HCO_3	18	$NH_4HCO_3 + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ + HCO_3^-$	2	1	12
$(NH_4)_3PO_4$	28	$(NH_4)_3PO_4 + 6O_2 \rightarrow 3NO_3^- + PO_4^{3-} + 3H_2O + 6H^+$	6	3	36
$(NH_4)_2SO_4$	21	$(NH_4)_2SO_4 + 4O_2 \rightarrow 2NO_3^- + SO_4^{2-} + 2H_2O + 4H^+$	4	2	24
NPK[a]	21	$(NH_4)_2HPO_4 + 4O_2 \rightarrow 2NO_3^- + HPO_4^{2-} + 2H_2O + 4H^+$	4	2	24
N deposition	—	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	2	1	12

[a]NPK: $(NH_4)_2HPO_4 + KCl$. Note that besides H^+ release by nitrification, plant N uptake as NH_4^+ and other cations also leads to H^+ release (not presented in this table).

the amount of N fertilizer lost by NH_3 volatilization that was not available for nitrification was subtracted from the equation. The annual NH_3 emission inventories compiled for China from 1980 to 2012 were taken from Kang et al. (2016) and were kept constant at 10% from 2012 until 2100.

The portion of N fertilizer taken up by crops (FNR) does not contribute to soil acidification directly but can have indirect effects (Figure 1). The remaining N undergoes nitrification and releases H^+. The FNR by crops in China from 1980 to 2010 was obtained from the study by Yan et al. (2014).

For N deposition, a similar ratio of NH_3 volatilization to FNR was used as that for N fertilizer.

Finally, based on theoretical assumptions, the potential of H^+ release by each N fertilizer type and atmospheric N deposition was calculated as well as their potential to dissolve $CaCO_3$ and release CO_2 (Table 1).

Based on the information above, two equations were developed (Equations 5 and 6) that were used to calculate $CaCO_3$ dissolution and the subsequent CO_2 efflux from soils for each year in each province of China from 1980 to 2100:

$$CaCO_3 - C \text{ dissolution (Tg)}$$
$$= \sum_{i=1}^{n} \{(N_{fert} + N_{dep}) - (FNR + N_{volat}) \times C\}, \quad (5)$$

$$CO_2 - C \text{ emission (Tg)}$$
$$= \sum_{i=1}^{n} \{(N_{fert} + N_{dep}) - (FNR + N_{volat}) \times C\}, \quad (6)$$

where n is the N fertilizer type, N_{fert} is the mineral fertilizer N input (Tg), N_{dep} is the atmospheric N deposition (Tg), FNR is the fertilizer N recovery (%), N_{volat} represents the NH_3 volatilization losses (%), and C is the conversion factor.

2.3 | Scenario analysis

Decreasing NUE and massive increases in N surpluses (227 kg N ha^{-1} $year^{-1}$) have made China a global N hotspot (Gu, Ju, Chang, Ge, & Chang, 2017). N fertilizer use in China increased at an average annual rate of 4% during 1980–2000 and at 2% during 2001–2015 (IFASTAT, 2020). Several studies have highlighted that N fertilization in China is well above crop requirements and there is great potential to decrease N rates without decreasing crop yield (Ju et al., 2009). The Chinese government is devising policies that focus on decreasing N fertilization, such as the Zero Increase Action Plan for Fertilizer Use (MOA, 2015). Based on the current N fertilization rate and the expected decrease in the future, the projected changes in $CaCO_3$ dissolution and CO_2 efflux from the soil were estimated under five scenarios of variable N fertilization rates, atmospheric N deposition, FNR, and NH_3 volatilization after 2020 (Table 2). The scenarios were as follows: (a) business as usual

(BAU; 1% annual increase in N input, 20% FNR); (b) S1 (15% lower N input than that of BAU, 30% FNR); (c) S2 (30% lower N input than that of BAU, 45% FNR); (d) S3 (no increase in N input, 55% FNR); and (e) S4 (1% annual decrease in N input, 65% FNR). The NH_3 volatilization losses were maintained at 10% in all scenarios after 2012.

Figures were prepared using SigmaPlot 12.5, and maps were created in ArcMap 10.3.

3 | RESULTS

3.1 | SIC stocks in Chinese provinces in 1980 and their relationship with soil pH

Total SIC stock at a 0–40 cm depth was 2.16 Pg C (16.3 Mg/ha) in croplands in China in 1980 and varied widely across provinces from 0.03 to 315 Tg C (0.01–70 Mg/ha; Figure 4). Provinces with minimum SIC reserves (<5 Tg C) were mainly located in the south of China (Fujian, Guangdong, Guangxi, Hainan, Jiangxi, Shanghai, Yunnan, and Zhejiang). The highest SIC stocks (>100 Tg C) were found in the north of China (Gansu, Inner Mongolia, Hebei, Henan, Shaanxi, Shanxi, and Xinjiang) including the Sichuan province.

The total cropland area of China was 132.5 million ha in 1980, of which 80.2 million ha (61%) had measurable $CaCO_3$ content in the soils (Figure 4; Table S2). The provinces where $CaCO_3$-containing soils covered over 80% of the total cropland area included Beijing, Gansu, Hebei, Inner Mongolia, Ningxia, Qinghai, Shanghai, Shanxi, Tianjin, and Xinjiang. Provinces in which $CaCO_3$-containing soils comprised less than 20% of the total cropland area included Fujian, Guangxi, Hainan, Yunnan, and Zhejiang.

SIC stocks increased exponentially with pH (Figure 5). The highest SIC stocks were common in soils with pH of 8–8.5 or above and decreased sharply at a soil pH threshold of less than 7.5. SIC stocks were absent in soils with pH below 6.5.

3.2 | $CaCO_3$ dissolution in Chinese croplands during 1980–2100

The total $CaCO_3$ dissolution in the 0–40 cm soil depth of Chinese cropland was estimated to be 145 Tg C (1.09 Mg/ha) during the past

TABLE 2 Detailed categorization of the various scenarios

N input and losses	BAU Business as usual	Scenario 1 15% Less N input of BAU	Scenario 2 30% Less N input of BAU	Scenario 3[a] Constant N input	Scenario 4 Decreasing N input
N input/year	+1%	−15% BAU	−30% BAU	0%	−1%
N recovery by crops	20%	30%	45%	55%	65%

[a]This scenario is in line with the policy of no increase in fertilizer consumption after 2020 (MOA, 2015). The NH_3 volatilization losses were maintained at 10% in all scenarios after 2012.
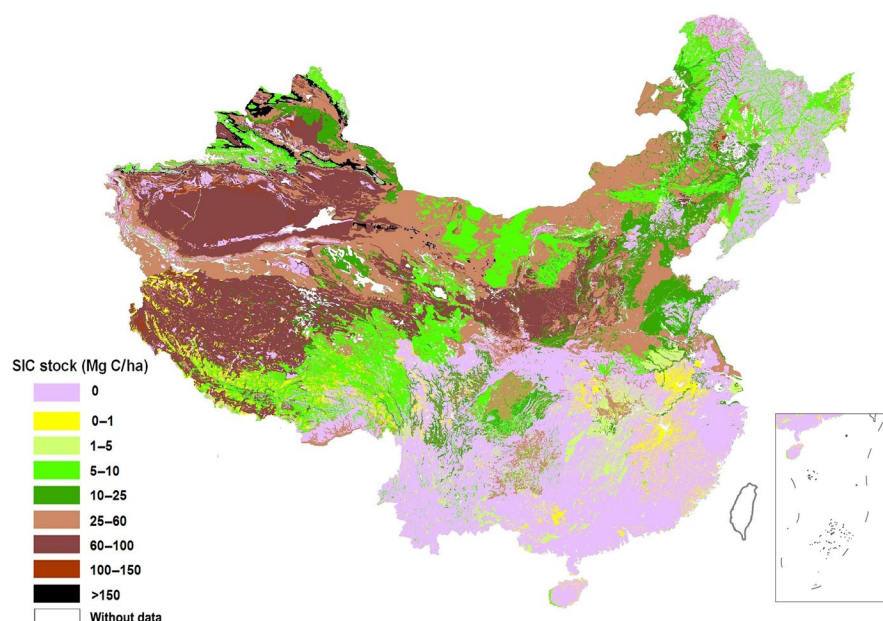
**FIGURE 4** Spatial distribution of soil inorganic carbon (SIC) stocks (Mg C/ha) in the 0–40 cm soil layer depth in China in 1980 [Colour figure can be viewed at wileyonlinelibrary.com]
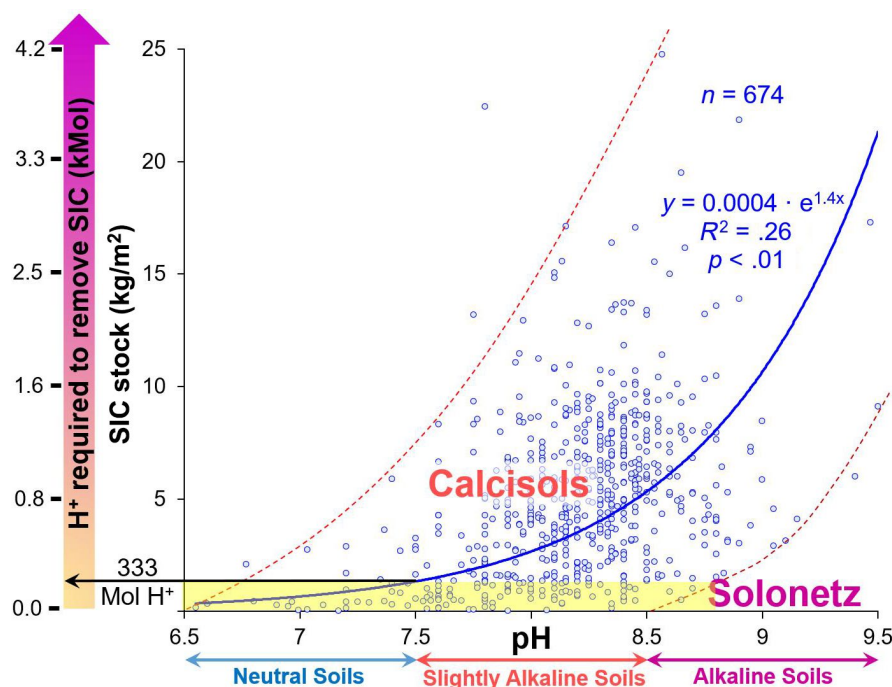

FIGURE 5 Relationship between soil pH (in H_2O; x-axis) and soil inorganic carbon (SIC, y-axis) stock in the upper 0–40 cm soil layer. The figure was prepared from the data obtained from the second national soil survey in 1980 (NSSO, 1994). The continuous blue line is the exponential regression curve. The soils with a pH lower than 6.5 do not contain any $CaCO_3$. The dashed red lines show the upper and bottom limits of $CaCO_3$ contents in the soils (envelope testing approach). The vertical arrow on the left shows the amount of H^+ ions (kMol) required to completely remove the respective SIC stock (kg/m^2). The soils in the yellow shaded area have on average <2 kg SIC/m^2. The addition of 333 mol H^+ will completely remove $CaCO_3$ from these soils. These are the soils that will lose $CaCO_3$ in the next 150 years if 15 g N m^{-2} year^{-1} (=150 kg N ha^{-1} year^{-1}) is nitrified every year. The two soil types Calcisols and Solonetz dominate these pH ranges but not exclusive of other soils [Colour figure can be viewed at wileyonlinelibrary.com]

40 years (1980–2020). The $CaCO_3$ dissolved at a rate of 2 Tg/year during 1980–2000 and at 5 Tg/year during 2001–2020 (Figure 6). Under the BAU scenario, $CaCO_3$ dissolution is further expected to increase up to 353 Tg (2.6 Mg/ha) until 2050, with a total C loss of 800 Tg C (5.9 Mg/ha) by 2100. $CaCO_3$ dissolution decreased the SIC stock. Since 1980 to date (2020), 7% of SIC stock in the upper 0–40 cm soil layer of croplands has been lost owing to nitrification-induced acidification. If the N input continues to increase in the same manner (BAU), China may lose 16% of its SIC stocks by 2050 and more than 37% by 2100 (Figure 6).
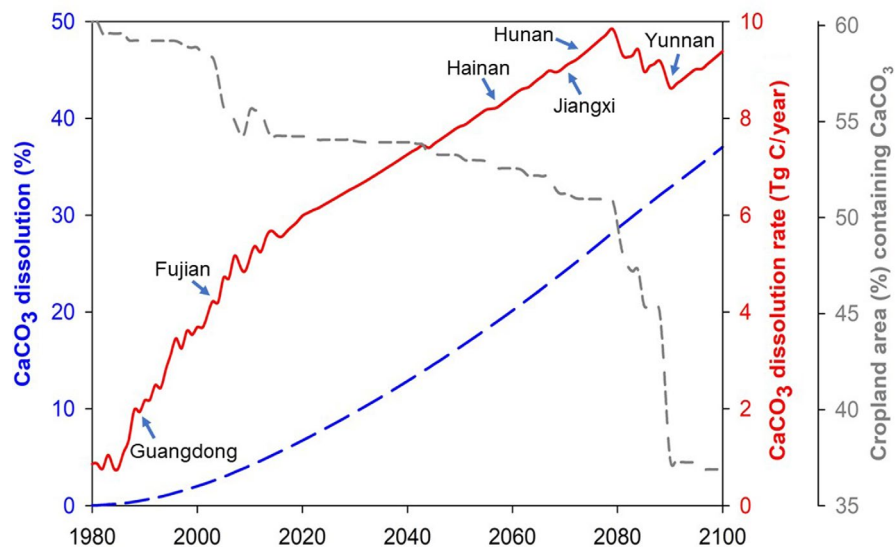
FIGURE 6 Dissolution of CaCO₃ stocks (% of CaCO₃ in the upper 40 cm), dissolution rate (Tg C/year) and changes in CaCO₃-containing cropland area from 1980 to 2020 (calculated) and estimated up to 2100 under the business as usual (BAU) scenario. A sharp decrease in CaCO₃ dissolution rates at various points occurred when a soil type(s) lost all its SIC reserves. The arrows denote the year of complete CaCO₃ depletion from the individual province. Please note that these sharp decreases are produced exclusively by consideration of the upper 40 cm: the CO₂ will still be further produced by SIC dissolution below 40 cm [Colour figure can be viewed at wileyonlinelibrary.com]
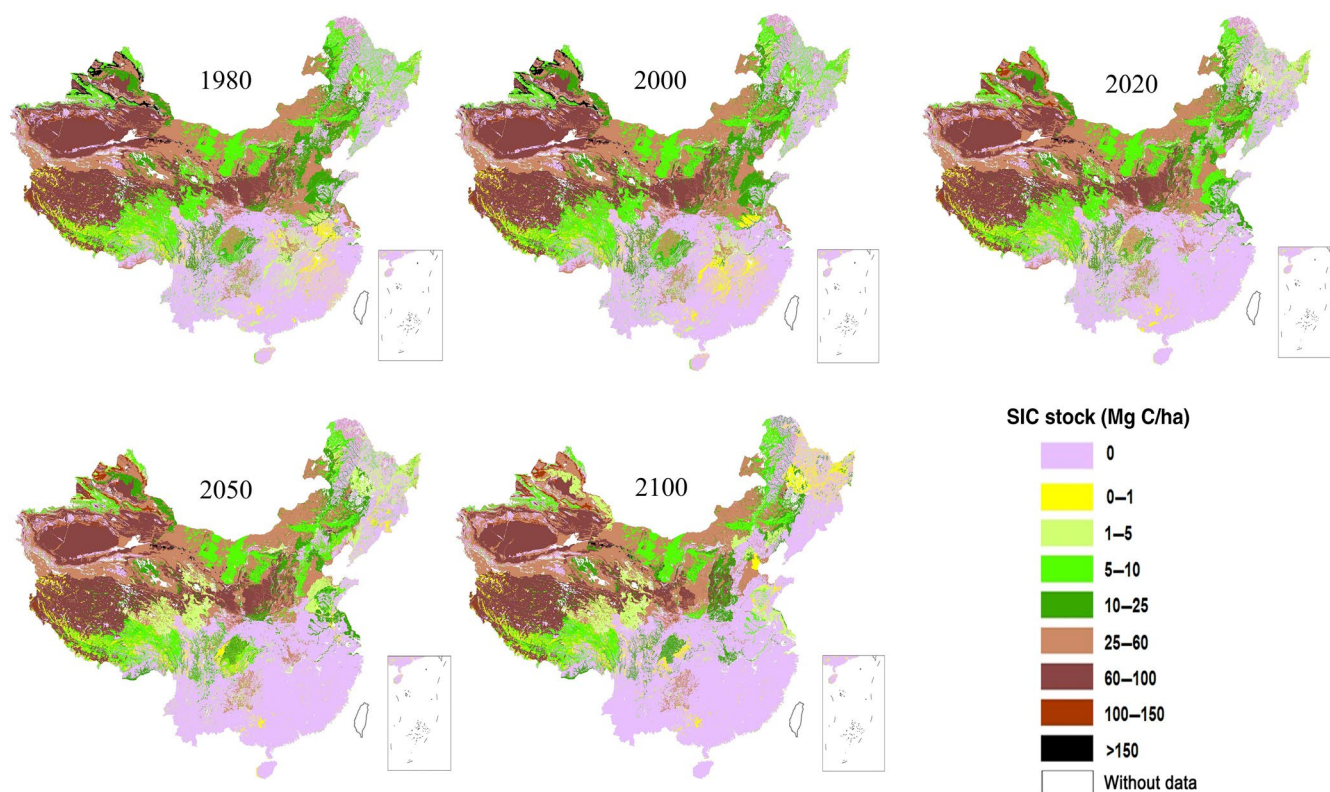
FIGURE 7 Spatial distribution of SIC stocks in China in the 0–40 cm soil layer depth in the past (1980 and 2000), ongoing (2020), and in future (2050 and 2100). The SIC stocks were measured from 1980 to 2020, and it was predicted from 2020 to 2100 under the business as usual (BAU) scenario. During 1980–2020, two provinces (Fujian and Guangdong) lost all their SIC reserves. During 2020–2100, SIC reserves were lost in four provinces (Hainan, Jiangxi, Hunan, and Yunnan). Note that the losses of SIC are ongoing and increasing at a rapid rate in the most productive cropland areas [Colour figure can be viewed at wileyonlinelibrary.com]

During 1980–2020, 7 million ha of cropland area (8.5%) of China has lost all SIC reserves (Figure 7). During this period, two provinces (Fujian and Guangdong) completely lost all their SIC reserves with

another three provinces (Guangxi, Hunan, and Jiangxi) losing greater than 75% of their SIC stocks. By 2100, 30 million ha of cropland area (37.8% of total cropland area) will be completely depleted of

SIC stocks. It was predicted that six provinces will lose all their SIC stocks and 11 provinces will lose greater than 65% of their stocks (Figure 7).

## 3.3 | CO_2 emissions from $CaCO_3$ dissolution during 1980–2100

CO_2 efflux from the soil due to $CaCO_3$ dissolution following N fertilization was estimated to be 0.53 Pg (3.6 Tg C/year) in China during 1980–2020 (Figure 7; Table S3). These CO_2 fluxes are expected to reach 0.76 Pg (8.9 Tg C/year) during the next 30 years (2020–2050) and 1.64 Pg (8.9 Tg C/year) by 2100. Among provinces, Hebei, Henan, Jiangsu, Shandong, Sichuan, and Xinjiang had the highest CO_2 efflux (>0.2 Tg C/year) from SIC dissolution during 1980–2020, whereas Fujian, Guangdong, Hainan, Qinghai, Tibet, and Zhejiang had the lowest rate of CO_2 efflux from SIC dissolution (<0.01 Tg C/year), mainly due to less cropland area present in the latter provinces. The predicted CO_2 losses until 2050 are expected to be 43%

higher than the C losses in 2020 and an approximately twofold increase is expected until 2100.

3.4 | Scenario analysis

$CaCO_3$ loss and subsequent CO_2 release were calculated and forecasted for various carbonate dissolution scenarios (BAU, S1, S2, S3, and S4) during 2020–2100. Compared to the BAU scenarios, 15%–30% decreased N input (S1 and S2) is predicted to decrease $CaCO_3$ dissolution among provinces by 18%–41% up to 2100 (Figure 8). If N input in China remains constant as of 2020 (S3), the $CaCO_3$ dissolution will be 52% lower than that in the BAU scenario. In S4, with an annual decrease of 1% in N input, there could be 67% lower $CaCO_3$ dissolution than that in the BAU scenario. A similar trend was observed for CO_2 efflux under the same scenarios (Figure 8).

During 1980–2100, 30 million ha cropland area is expected to lose its $CaCO_3$ stock in the BAU scenario. Decreasing N fertilizer
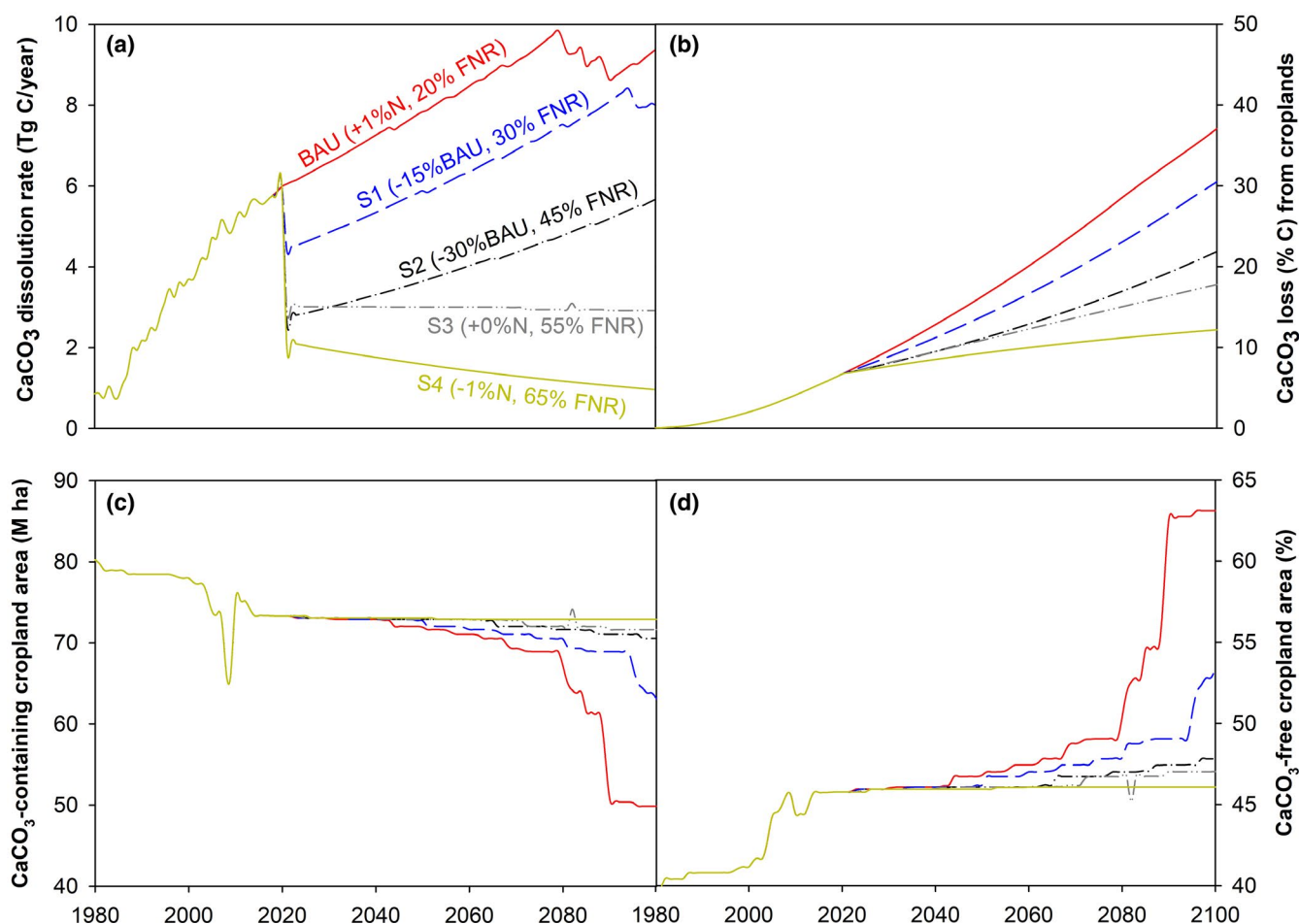
FIGURE 8 Changes in $CaCO_3$ dissolution rate (Tg C/year; a), total $CaCO_3$ dissolution (%; b), carbonate-containing cropland area (million ha; c), and cropland area (%) without $CaCO_3$ (d) in China under five scenarios during 1980–2100. The $CaCO_3$ content in 1980 was used as a baseline (100%; b) and loss in $CaCO_3$ was calculated from this point onward. The NH_3 volatilization losses were maintained at 10% in all scenarios after 2012. FNR is the fertilizer N recovery by crops. The sharp decrease of $CaCO_3$-containing cropland area in (c) in 2008–2009 is not necessarily due to soil acidification, but rather due to an overall decrease in the cropland area [Colour figure can be viewed at wileyonlinelibrary.com]

input by 15%–30% (S1 and S2) will save $CaCO_3$ stock on 13–21 million ha (Figure 8). This will further increase to 22–23 million ha in S3 and S4 scenarios.

4 | DISCUSSION

4.1 | Acidification induced $CaCO_3$ losses from cropland soils in China

To the best of our knowledge, this is the first study quantifying carbonate dissolution from Chinese croplands because of N fertilization-induced soil acidification. $CaCO_3$ loss by acidification was estimated to be 145 Tg C (7% of the $CaCO_3$ stock in 1980) during the last four decades (1980–2020), which corresponds to an annual loss of 3.6 Tg C from 7 million ha of cropland (Figure 6). These losses decrease the SIC stocks, and five provinces (Guangdong, Fujian, Guangxi, Hunan, and Jiangxi) that had low inherited SIC stocks have already lost more than 75% of their SIC stocks from the upper 40 cm soil layer (Figure 7). If N fertilizer use continues to increase at the same rate as the present (BAU scenario), 30 million ha of cropland area will be on the verge of complete $CaCO_3$ depletion by 2020–2100 owing to acidification, which includes the complete depletion of SIC from six provinces and another 11 provinces losing greater than 65% of their SIC stocks. Because N fertilization rate is much higher in orchards and vegetable systems than in croplands, soil acidification is much faster, and subsequent SIC depletion is expected to be more intensive compared to croplands (Gu et al., 2017; Yan et al., 2012). Acidification rates and SIC depletion are comparatively lower in grasslands because of very low N fertilization rates (Yang et al., 2012).

Several studies have highlighted significant amounts of SIC losses from acidification worldwide (Zamanian & Kuzyakov, 2019; Zamanian et al., 2018). The results of the Rothamsted long-term study showed that N fertilization- and deposition-induced $CaCO_3$ dissolution decreased carbonate content in the topsoil from 5% in 1865 to less than 1% in 1966 (Bolton, 1972). A long-term study in the North China Plain has shown that high fertilizer inputs have decreased the carbonate content in the topsoil from 2.3% to 3.9% in 1981 to a mean of 0.8% in 2009 (Heimann et al., 2015). Another long-term study in southwest China showed that carbonates were consumed after 25 years of ammonium fertilization, and soil pH decreased from 7.7 in 1990 to 6.0 in 2013–2015 (Zhang, Vries, Thomas, Hao, & Shi, 2017). Soils in the Yangtze River delta had considerable amounts of carbonates in the 1980s but showed no carbonates or low carbonate contents by 2003 (Wang, Li, et al., 2015). Similarly, the annual acid input of 0.5–34 kmol H^+ ha^{-1} $year^{-1}$ resulted in an average CO_2 emission of 145 kg ha^{-1} $year^{-1}$ owing to the dissolution of carbonates from various soils and land uses in Australia (Ahmad, Singh, Dalal, & Dijkstra, 2015). All these studies confirm that SIC loss from dissolution of carbonates is ongoing and very rapid. Increasing N fertilization and atmospheric deposition is common in many countries, which makes acidification-induced SIC loss a global concern (Zamanian et al., 2018). Therefore, it is very urgent for soil acidification to be restrained by decreasing N fertilizer input and improving its efficiency.

4.2 | Removal of carbonates is a threat to soil fertility and crop productivity

Soil pH and SIC content are positively correlated (Figure 5). $CaCO_3$ dissolution and loss while buffering H^+ is harmful to soil health and crop productivity (Table 3). Decalcification decreases SOM stability by decreasing the binding of organic matter on Ca^{2+} (Rowley, Grand, & Verrecchia, 2018). $CaCO_3$ dissolution drives the loss of base cations (Ca^{2+}, Mg^{2+}, and K^+) and subsequently decreases soil fertility (Zhang et al., 2016). The accelerated loss of base cations decreases the availability of exchangeable Ca^{2+}, Mg^{2+}, and K^+ by 24% (Lucas et al., 2011). The 100-year experiments at Rothamsted showed that continuous N fertilization strongly decreased the content of exchangeable Ca^{2+} and Mg^{2+}, and plants exhibited nutrient-deficiency symptoms (Bolton, 1972; Bolton & Slope, 1971). Base cations once removed from the soil move with water and can negatively influence fresh water quality and aquatic life by salinization and alkalinization (Kaushal et al., 2018). A long-term study at the catchment scale found that acidification resulted in increased base cation riverine exports (Aquilina et al., 2012).

Soil pH remains stable at approximately 8, when $CaCO_3$ content is higher than 2% but decreases sharply (from 8.0 to 6.0) as $CaCO_3$ content falls below 1% (Wang, Li, et al., 2015). There is a nonlinear relationship between soil pH and SIC stock (Figure 5). The acid-neutralizing rate of other buffer systems below pH 6.5 is very slow (except base cation exchange), and their neutralizing capacity depends on the composition of clay minerals and soil parent material (Figure 2). Soil pH below 6.5 decreases the microbial biomass, activity, and respiration, and increases the fungal-to-bacterial ratio (Rousk et al., 2010; Tian et al., 2019). At a low pH (≤4.0), there is a significant increase in the mobility and bioavailability of heavy metals. A nationwide survey in China showed that soil acidification is a major driver of heavy metal pollution, which has contaminated 19% of agricultural croplands (Zhao, Ma, Zhu, Tang, & McGrath, 2014). Winter wheat grains grown in the carbonate-free soils of the Yangtze River delta have three times as much nickel and twice as much cadmium content relative to wheat grains harvested from carbonate-containing soils (Wang, Li, et al., 2015). Further pH decreases also mobilize and release free Al^{3+} and Fe^{3+} chelates and Fe^{2+} into the soil solution. The deficiency of certain plant nutrients (Ca^{2+}, Mg^{2+}, Na^+, K^+) and an excess of aluminum seriously affect nutritional balance, which severely decreases root growth, and the yield and quality of crops (Goulding, 2016). Based on the pH–yield relationship, the increasing soil acidification decreased cereal yields by 4% in China from 1980 to 2010, which may decrease up to 24% by 2050 if acidification from N fertilization continues to increase at the same rate as the present (Zhu et al., 2020). Therefore, producing healthy food from rapidly depleting carbonate soils will be a greater challenge in the future.

4.3 | Implications and practical recommendations

Our findings have important implications for scientists, land managers, and policy makers. It is often assumed that SIC stocks are very

TABLE 3 Direct and indirect effects of optimal $CaCO_3$ contents (2%–15%) on physical, chemical, and microbiological soil processes and properties as well as plant nutrition and productivity[a]

Soil and plant processes	Direct $CaCO_3$ effects	Indirect $CaCO_3$ effects[b]
Physical properties and soil structure	• Aggregate formation and stability • Lower bulk density	• Improved soil structure • High water holding capacity • Lower bulk density • Good aeration and water permeability • Decreased erosion
Chemical properties	• Strong buffering capacity • Cation bridging for organic matter stabilization	• Decreased leaching of base cations • Good nutrients availability (*except P Fe, Zn*) • High organic matter stability • Absence of clay mineral weathering
Microbial properties		• Higher microbial abundance and activity • Balanced bacteria:fungi ratio • Fast but incomplete decomposition of plant residues → soil organic matter formation
Plant nutrition and productivity	• Very good Ca^{2+} nutrition • *Decreased P availability*	• Improved plant growth • Good and deep root penetration • Maximal availability of most nutrients (*except P, Fe, Zn*) • *Low physiological K^+ availability is possible* • Better resistance to pathogens and abiotic stresses

[a]Negative effects are presented in *italics*.

[b]The most indirect effects of $CaCO_3$ in soil relate to the optimal pH.

stable, and thus play only a minor role in the short-term global terrestrial C cycle. However, global soil acidification leads to SIC dissolution (Tian et al., 2019; Zamanian et al., 2018) and, consequently, this C will be released into the atmosphere and contribute to global warming. Therefore, N fertilization-induced SIC dissolution should be incorporated into regional C budgets and models that predict C cycling in terrestrial ecosystems (Yang et al., 2012; Zamanian & Kuzyakov, 2019; Zamanian et al., 2018). Without considering SIC dissolution, our understanding of the terrestrial C cycle and its feedback to climate change are incomplete.

The analysis of inorganic C and cations such as Ca^{2+} in soil is generally not carried out on a routine basis. As $CaCO_3$ depletion is occurring at an increasing rate; SIC and base cations are suggested to be included in soil testing manuals, particularly for those areas where their contents are rapidly decreasing. This will provide important information regarding buffering capacity, soil degradation, and threats of heavy metal dissolution under severe acidification. Training and education of farmers regarding the detrimental effects of soil acidification on crop production is required.

Acidification problems of soils in China are associated with high N surplus (>200 kg N ha^{-1} year^{-1}) and decreasing NUE. Increasing NUE to 50% could cut N fertilizer use by 6.6 Tg/year in China (41% of the total N used; Huang & Tang, 2010). Therefore, improving NUE and decreasing N fertilization would directly decrease soil acidification and carbonate loss. The decreasing N input and improved NUE scenarios (S1–S4) would also decrease $CaCO_3$ loss by 18%–67% in China (Figure 8). However, even if N fertilization is decreased, $CaCO_3$ loss will still occur because acidification is a natural phenomenon driven by several processes (Figure 1).

N fertilization should be performed strictly based on the crop requirements while also considering the amount of residual N that is available to the crops. Enhanced efficiency additives, such as urease and nitrification inhibitors, retard acidification and, therefore, should be incorporated with N fertilizer (Raza et al., 2019). Crop and livestock farms should be integrated with a major focus on effectively reusing crops and animal waste. The addition of crop residue-derived biochar and manure is beneficial, as they temporarily increase the pH as well as buffering capacity of the soil (Shi et al., 2017, 2019; Wu et al., 2018). The application of lime should be regularly practiced in carbonate-depleted soils to avoid further soil degradation and fertility decrease. Finally, N uptake by crop cultivars could be improved by introducing genes that are responsible for effective N utilization (Yadav et al., 2017). All these management practices will leave less N in soil and, consequently, decrease and prolong anthropogenic-induced acidification.

4.4 | Sources of uncertainty

There are several uncertainties associated with the estimated $CaCO_3$ dissolution. First, the $CaCO_3$ dissolution and subsequent CO_2 emissions were estimated based on H^+ that was released only from N fertilization and N deposition. The contribution of H^+ input from other acidifying processes mentioned in Figure 1 was not considered. Considering all acidification processes, the $CaCO_3$ dissolution rate should be more rapid than our estimation. High precipitation also facilitates $CaCO_3$ loss from the topsoil (Yang et al., 2012); however, this was not considered in the present study.

Second, SIC losses were estimated only from the upper 40 cm. Many soils that are free of carbonate in the top 40 cm still have substantial $CaCO_3$ stocks in their deeper layers (Figure 7). Consequently, at least part of the produced H^+ ions will be leached below 40 cm and neutralized by $CaCO_3$ consumption with subsequent CO_2 release. As the majority of the $CaCO_3$ stocks are found below 40 cm (Zamanian, Pustovoytov, & Kuzyakov, 2016), their complete dissolution and CO_2 release could take centuries or even millennia to occur.

Third, $CaCO_3$ dissolution was calculated based on H^+ input from total N input for each province. However, there are some hotspots of very intensive agriculture (e.g., orchards and greenhouse vegetables) within each province, where N fertilizer use is much higher and, therefore, have a much stronger local influence on soil acidification and $CaCO_3$ dissolution. Long-term manure application increases soil resistance to acidification induced by N fertilization over short periods and hence can reduce subsequent $CaCO_3$ dissolution (Shi et al., 2019).

Finally, we only focused on $CaCO_3$ dissolution and loss from the soil as CO_2. A part of the dissolved $CaCO_3$ may later reprecipitate in the soil, for example, during drought conditions (Sanderman, 2012). SIC can also increase by trapping CO_2 coming from mineralization of organic matter and root respiration in alkaline soils (Guo et al., 2016; Wang, Wang, et al., 2015; Xie et al., 2009; Zhao et al., 2016). $CaCO_3$ dissolution and precipitation depends on many factors, including Ca^{2+} availability, CO_2 partial pressure in the soil, pH, and moisture. Therefore, more field-scale and regional studies are needed to evaluate the changes in SIC stocks and its subsequent effects on soil health and plant productivity.

5 | CONCLUSIONS

$CaCO_3$ dissolution from N-induced soil acidification has depleted 145 Tg C (1.1 Mg/ha) of SIC stocks from Chinese croplands during the past four decades (1980–2020). The unaccounted CO_2 released from this dissolution was estimated to be 0.53 Pg (3.6 Tg C/year). From 1980 to 2020, five provinces have lost more than 75% of their SIC stocks. By 2100, six more provinces will lose all their SIC stocks, and 11 provinces will lose more than 65% of their SIC stocks. Increases in the unaccounted CO_2 release and Ca^{2+} loss from SIC dissolution are posing significant threats to the future sustainability of Chinese crop production systems. Therefore, monitoring the pH and carbonate content in soils is recommended, especially in areas with low carbonate levels.

Our scenario analysis indicated that $CaCO_3$ dissolution could be decreased compared to the BAU scenario by up to 52%–67% if N input in China remains constant or will decrease by 1% annually. There is a great need to rethink N fertilization policies and strategies. Measures involving decreasing N fertilizer input (S4) and improving NUE must be adopted. Crops should be fertilized according to their demand while considering the residual N availability in the soil. Integrated nutrient management practices involving N input from various sources (i.e., organic and mineral) should be adopted to avoid soil acidification, $CaCO_3$ losses, and CO_2 release.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request. Supporting information is also available as supplementary material.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Raza S, Miao N, Wang P, et al. Dramatic loss of inorganic carbon by nitrogen-induced soil acidification in Chinese croplands. *Glob Change Biol.* 2020;26:3738–3751. https://doi.org/10.1111/gcb.15101