



Inorganic carbon losses by soil acidification jeopardize global efforts on carbon sequestration and climate change mitigation

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ABSTRACT

Soil plays a significant role in controlling the global carbon (C) cycle. Studies on climate change mitigation have focused entirely on soil organic carbon (SOC) to increase C sequestration and decrease carbon dioxide (CO_2) emissions. In contrast, the contribution of soil inorganic carbon (SIC) to CO_2 emissions is usually neglected because SIC is generally considered to be very stable. However, the significant worldwide increase in soil acidification, mainly because of intensive N fertilization and high atmospheric deposition, causes a considerable decrease in SIC stocks, leading to very high unaccounted CO_2 efflux. Additionally, large areas of acidic soils worldwide are regularly subjected to high SIC applications in the form of lime to remediate acidity, which is another direct source of CO_2 emission. Consequently, global efforts to mitigate climate change through SOC sequestration need a revisit as SIC-borne C losses are significant both in terms of C stocks and soil fertility loss, upon which future SOC sequestration will be reduced. Compared to SOC, wherein C stocks can be increased through management, SIC losses are irreversible and cause significant decline in soil health, ecosystem services, and functions. The present review is the first to summarize the current information about acidification-induced intensified SIC losses and their mechanisms. It included: (i) natural and anthropogenic sources and causes of soil acidification, (ii) losses of SIC as HCO_3^- leaching and CO_2 efflux from calcareous soils (7.5 Tg C yr^{-1}) and liming (273 Tg C yr^{-1}) during acidity neutralization, (iii) the relationship between climate change and SIC stocks, (iv) consequences of SIC depletion in soil-plant-water systems, and (v) strategies to remediate and control soil acidification. We concluded that acidification-induced SIC-borne CO_2 losses are a major C loss pathway and could jeopardize global efforts to mitigate climate change through SOC sequestration.

1. Introduction

Climate change is currently one of the biggest challenges for humanity. Increases in greenhouse gas (GHG) emissions are the major drivers of global warming and climate change. Carbon dioxide (CO_2) accounts for more than 70% of the total anthropogenic GHG emissions (Ahmad et al., 2020). Soil is the largest terrestrial carbon (C) reservoir within the biosphere, with approximately thrice the amount of C as that in living plants and twice that in the atmosphere (Schlesinger, 1990, 1995). Consequently, even a small change in the soil C pool can have a

substantial impact on atmospheric CO_2 concentration and subsequent global warming (Davidson and Janssens, 2006; Trumbore and Czimczik, 2008).

The soil C pool comprises two distinct components: soil organic C (SOC) and soil inorganic C (SIC). The estimated size of SOC is $1500\text{--}1600 \text{ Pg}$ ($\text{Pg} = 10^{15} \text{ g}$) at 1 m depth (Batjes, 1996; Monger and Gallegos, 2000; Lal, 2004). SOC is a ubiquitous feature of all soils and is considered the main pool driving C flux and sequestration (Lal, 2004; Sanderman and Baldock, 2010). Soils have enormous potential to mitigate climate change through SOC sequestration, driven by

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photosynthetic CO₂ fixation and belowground allocation. Therefore, most previous studies have focused on SOC as a climate mitigation strategy, including a recently launched (but scientifically unverified and still under debate) initiative of “4 per 1000” (4p1000) at the COP21 conference in Paris (<http://4p1000.org>), which aims at a yearly increase of 4% (0.4%) in global SOC stocks (Rumpel et al., 2020).

The size of SIC ranges from 695 to 1738 Pg worldwide (Eswaran et al., 1995; Batjes, 1996). Inorganic C as soil carbonate (~940 Pg C) and as bicarbonate in groundwater (~1404 Pg C) together surpassed SOC (~1530 Pg C) as the largest terrestrial C pool (Monger et al., 2015). The global SIC pool is primarily located in arid and semi-arid regions, accounting for 90% of the total soil C stocks (Filippi et al., 2021). Calcareous soils account for approximately 50% of the Earth's surface and approximately 9 billion hectares of arable land worldwide (Marschner, 1995; Lal, 2009). Soil inorganic C is generally disregarded as a C stock compared to SOC, because it is assumed to be much more stable and less sensitive to agricultural activities within the human life timescale (Sanderman, 2012). However, recent studies have clearly shown that agricultural practices cause a rapid drop in the SIC pool. Soil acidification, water flow and recharge, and land-use changes can decrease SIC stocks within a few decades (Kim et al., 2020; Liu et al., 2020; Raza et al., 2020). Even deep SIC stocks (at 7 m below ground) are vulnerable to loss through agricultural practices that are generally considered as stable for millennia (Kim et al., 2020). Carbon losses from this massive pool and their contribution to global climate change are generally neglected.

Intensive agricultural practices and high nitrogen (N) fertilization rates acidify soils worldwide (Guo et al., 2010; Zamanian et al., 2018; Raza et al., 2020). Soil acidification affects up to 40% of arable soils worldwide, and more than 70% of potential arable land (Von Uexküll and Mutert, 1995). Calcareous soils have a strong buffering capacity to counteract the acidification. In these soils, SIC pools exchange C with the atmosphere owing to the neutralization of mineral acidity. In this process, SIC is released to the atmosphere as CO₂, or leaches into the soil profile, where it can reprecipitate to form pedogenic carbonates (Lal and Kimble, 2000; Lal, 2008), or enters groundwater in the form of HCO₃⁻. Losses of SIC as CO₂ efflux are occurring at a rapid scale (7.5 Tg C yr⁻¹), accelerating global warming and climate change (Bertrand et al., 2007;

Tamir et al., 2011; Zamanian et al., 2018). In addition to these SIC losses from calcareous soils, large areas (up to 3.8 billion hectares) of acidic soils are regularly limed to alleviate adverse effects of acidification, which also release CO₂ during neutralization (Zamanian et al., 2018, 2021).

This review focused on the dynamics of SIC losses from calcareous and limed soils in response to intensified acidification. To provide a logical framework for these processes, we first described the natural and anthropogenic sources of acidification, followed by their impact on acidification and acidity neutralization, SIC dissolution, and CO₂ efflux. The vulnerability of SIC losses in response to global climate change and the consequences of carbonate losses for soil-plant-water systems are extensively discussed. We also explored the problems associated with liming and proposed new methods to control soil acidification, which are helpful in stabilizing SIC stocks. Finally, several perspectives in terms of further research on SIC dynamics are presented to address questions that remain poorly understood and/or are highly debatable.

2. Sources and drivers of soil acidification

Soil acidification occurs when acidity-generating processes offset acidity-consuming processes. Moreover, the various ways by which H⁺ ions are added to the soil (Fig. 1) can be broadly classified as natural and anthropogenic sources.

2.1. Natural drivers of soil acidification

Under natural conditions, acidification is mainly induced by (i) biological N fixation (BNF) of atmospheric N₂, (ii) oxidation of soil organic matter (SOM), (iii) cation uptake by plants and removal by harvest, (iv) release of organic acids by roots, (v) oxidation of N₂ to NO_x by lightning, and (vi) volcanic eruptions (Fig. 1). Other natural causes of acidification include dissolution of CO₂ (originating from respiration of roots and microbes by SOM decomposition) to form HCO₃⁻ and the synthesis and dissociation of carboxylic acids produced by plants and microorganisms. High precipitation (>600–800 mm) facilitates acidification because rainfall is naturally acidic (pH: 5.0–5.5) and causes dissolution and leaching of basic cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺)

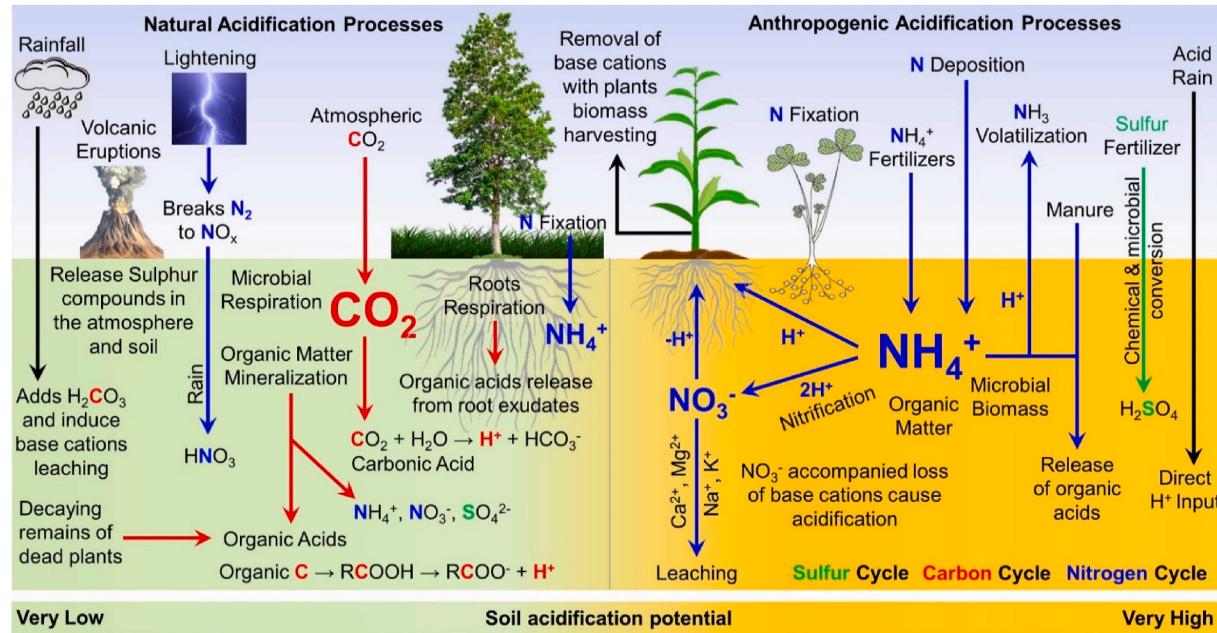
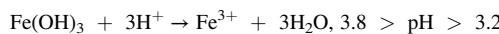
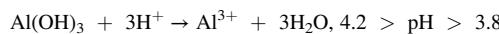
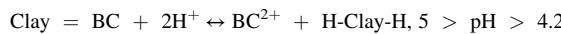
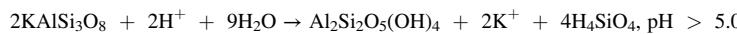
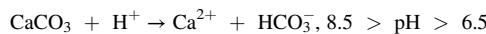
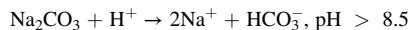


Fig. 1. Natural and anthropogenic processes causing soil acidification. Blue, red, and green text and arrows represent acidity-generating processes from N, C, and S cycles, respectively. Black arrows represent acidification from processes other than the cycling of these three nutrients. The light green color on the left shows lower acidification potential of natural processes, whereas the orange color on the right shows higher acidification potential of anthropogenic processes.

(Lucas et al., 2011). Lightning also adds H⁺ ions to the soil by facilitating the formation of nitric acid through the reaction of atmospheric N, oxygen, and water (Fields, 2004). Natural soil acidification processes are very slow, extending over centuries or millennia, and acidification rates depend on the chemistry of parent materials and the annual water balance (precipitation vs. potential evapotranspiration) (Sumner and Noble, 2003).

2.2. Anthropogenic drivers of soil acidification

Human activities have significantly perturbed the global N cycle more than the global C cycle (Erisman et al., 2015; Battye et al., 2017), even beyond the “planetary boundary” (Steffen et al., 2015). Reactive N inputs to soils have more than doubled compared to the pre-industrial natural N amounts produced in terrestrial ecosystems (Gruber and Galloway, 2008). In addition to substantial increases in N fertilizer input (from 12 to 108 Tg yr⁻¹), other sources such as manure, BNF, and atmospheric N deposition (from 6 to 10 Tg N yr⁻¹) have significantly increased during the past six decades. However, N use efficiency (NUE) has strongly decreased, leading to strong acidification of soils worldwide (Fig. 2; Guo et al., 2010; Zamanian et al., 2018; IFASTAT, 2020; Raza



et al., 2020).

Currently, plants utilize less than half of the total N input worldwide, which implies that more than half are released to the environment (Fig. 2; Lassaletta et al., 2014). This imbalanced and inefficient use of reactive N by crops, and removal of plant biomass and base cations by harvest have increased acidification rates worldwide over the past few decades, particularly in China (Guo et al., 2010; Hao et al., 2019; Zhu et al., 2020). The major process leading to acidification during the N cycle is nitrification. As shown in Equation 1, nitrification of 1 mol of ammonium to nitrate releases 2 mol of H⁺ ions.



Ammonium-based fertilizers account for 72% of the total N fertilizer input worldwide (Fig. 2; IFASTAT, 2020). The nitrification-driven acidification rate is approximately 10–100 times faster than that of acid deposition (Guo et al., 2010). Nitrogen addition increases microbial activity, which increases the mineralization of organic N and releases NH₄⁺, which then undergoes nitrification and causes acidification. In poorly aerated soils, the nitrification process is very slow; hence, increased NH₄⁺ uptake by roots releases H⁺ ions into the soil solution. Nitrate is also a source of acidity because it is highly mobile and Ca²⁺, Mg²⁺, and other base cations are lost during leaching to maintain charge balance (Fernandez et al., 2003). Consequently, N fertilization produces acidity even in the absence of nitrification (Zamanian et al., 2018).

In summary, all acidification processes, particularly N fertilization and atmospheric deposition, have significantly reduced soil pH worldwide over the past few decades. At present, 3.79 billion hectares of the world's area is acidic, and 2.04 billion hectares is under acidification risk because of continuous increase in N fertilization-induced

acidification (Zamanian et al., 2018).

3. Soil buffering systems and the importance of carbonate in buffering pH

Soil acidification is a continuous and ongoing process in both natural and managed systems. All soils have buffering systems to resist acidification, which depends on intrinsic properties, such as parent material, cation exchange capacity (CEC), soil texture, and mineralogy (Bowman et al., 2008; Yang et al., 2012). Buffering systems differ in their acid neutralization capacities and functions at a specific pH range (Fig. 2). When the pH is above 8.5, soil acidification is largely buffered by sodium carbonate (Equation 2). At pH 6.5–8.5, the H⁺ input is balanced by carbonates and carbonates, leading to the leaching of HCO₃⁻, Ca²⁺, and Mg²⁺ (Equation 3). In slightly acidic soils (pH: 5.0–6.5), weathering of silicate minerals contributes to most of the buffering capacity (Equation 4). The soil CEC buffers further decrease in pH by the exchange of base cations (BC; Ca²⁺, Mg²⁺, K⁺, and Na⁺) from the mineral and organo-mineral particles (Equation 5). When the soil pH is below 4.2, the pH change is buffered by the dissolution of aluminum oxides and then, at a pH of approximately 3 by iron hydroxides (Equations 6 and 7).

Carbonates provide the strongest buffering system and maintain the soil pH above 6.5 (Fig. 3; Kuzyakov et al., 2021). The added H⁺ fully neutralizes, and the pH of the soil solution remains relatively constant and/or decreases very slowly from 8.5 to 6.5 in the presence of carbonates (Fig. 3). Soils acidify rapidly in the absence of carbonates because the buffering capacities of other systems are weaker or slower (Fig. 2). At present, many soils are losing their acid-neutralizing capacity owing to a consistent increase in H⁺ input and subsequent decrease in the acid neutralizing mediators (carbonate and cations) (Raza et al., 2020).

4. Soil inorganic C depletion and CO₂ emissions from calcareous and limed soils

4.1. Decreases in SIC stocks and CO₂ emissions from calcareous soils

Intensified acidification from intensive agricultural practices, particularly the high inputs of N fertilizers, causes increased SIC losses worldwide (Table 1), mainly as CO₂ efflux, and as leaching of bicarbonate at greater soil depths (Zamanian et al., 2018; Raza et al., 2020).

In the longest field experiment conducted in 1843 at Rothamsted, United Kingdom (Bolton, 1972; Poulton, 1996), the topsoil originally contained 5% carbonate at a pH value of approximately 8. By the 1940s, CaCO₃ was entirely lost from high N fertilization plots, followed by a rapid decline in pH. A long-term experiment in the North China Plain showed that high N applications reduced carbonate content from 2.3 to 3.9% in 1981 to 0.8% (average) in 2009 (Heimann et al., 2015). China

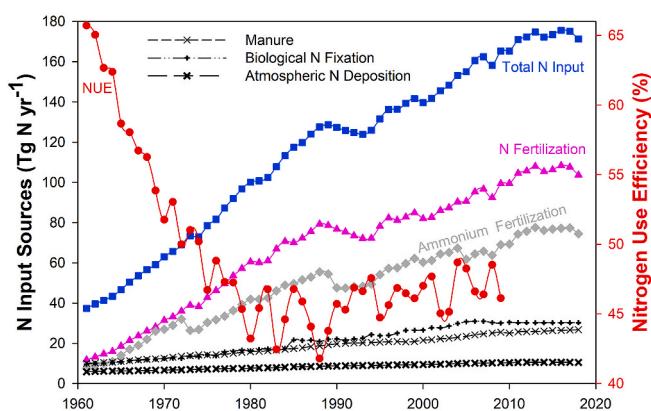


Fig. 2. Global temporal changes in reactive N input from various sources and NUE from 1960 to 2018 (Lassaletta et al., 2014).

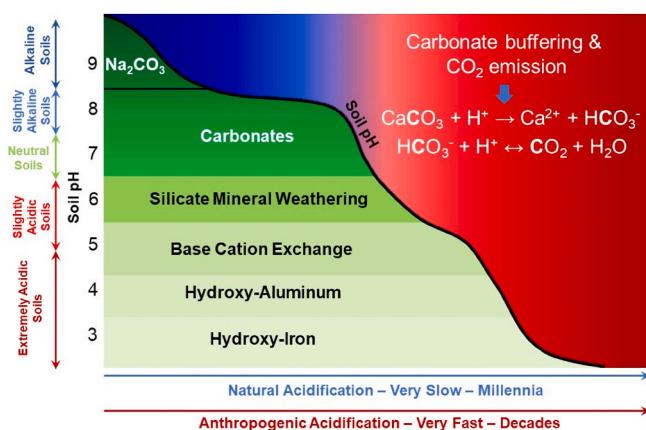


Fig. 3. Temporal changes in soil pH (Y axis) and buffering systems under natural and anthropogenic acidification (X axis). The blue-red area above the black curve shows intensity of soil acidity and the green gradients below the black curve show the acid neutralizing capacity of buffering systems. The two chemical equations at the top show the dissolution reactions of carbonate with soil acidification (H^+ input).

has lost 7% of the total CaCO_3 stocks (in the top 0–40 cm soil layer) due to acidification induced by N fertilization, which resulted in the loss of 145 Tg C as CO_2 during the last four decades (1980–2020) (Raza et al., 2020). Another 30 million hectare of cropland is expected to be free from carbonate by 2100 if increases in N fertilization remain the same (Raza et al., 2020). On a global scale, N fertilization-induced acidification causes SIC losses of 7.5 Tg C yr^{-1} in the form CO_2 (Zamanian et al.,

2018; Zamanian and Kuzyakov, 2019).

Owing to intensive agricultural practices, the rate of CaCO_3 loss from cultivated soils can be up to 10 times faster than that from natural soils (Magaritz and Amiel, 1981). In a recent agroforestry trial experiment, the proportion of CO_2 emissions from SIC in the 0–30 cm soil layer was observed to be 15–30%, which further increased up to 50–70% for 30–100 cm and 160–180 cm soil layers, respectively (Cardinael et al., 2019). Grasslands in China, which are generally not fertilized, have lost an average of 268 kg SIC $\text{ha}^{-1} \text{ yr}^{-1}$, which is mainly attributed to the acidification caused by the deposition of N and sulfur (Yang et al., 2012). Shrub encroachment in the grasslands of Inner Mongolia Plateau has decreased soil pH (0.17 units), mainly due to nitrification of biologically fixed N and base cation leaching with high moisture. This acidification decreased SIC density ($3.85 \pm 0.94 \text{ kg C m}^{-2}$) in the shrub-encroached grasslands compared to grassland without shrubs ($4.74 \pm 1.05 \text{ kg C m}^{-2}$) (Liu et al., 2020). These SIC losses mainly occur as CO_2 releases into the atmosphere instead of redistribution into deeper soil layers (Liu et al., 2020). Similar decreases in pH have been obtained in Tibetan grasslands with invasive shrubs (Gao et al., 2019). Invasion of non-native plant species in the native grasslands for 8 years has decreased SIC stocks by 250 g C m^{-2} mainly through acidification caused by the release of carbonic acid and carboxylic acids by root and microbial exudates (Wilsey et al., 2020).

In addition to acidification, other factors such as soil erosion, high rainfall intensity (soil moisture), and land-use changes also decrease SIC stocks from natural and agroecosystems (Yang et al., 2012; Kim et al., 2020; Liu et al., 2020). A comparison of cultivated and non-cultivated soils has revealed that approximately 1.6 Pg SIC was lost from 51% of cultivated soils in China during the past three decades, mainly due to land-use activities and fertilization (Wu et al., 2009). Kim et al. (2020) evaluated SIC dissolution scenarios to investigate soil water storage and transport resulting from cultivation practices, and found that SIC content was negatively correlated with groundwater recharge. Irrigated and rainfed croplands exhibited lower SIC storage of 730 Mg C ha^{-1} and 328 Mg C ha^{-1} , respectively, compared to their native vegetation (woodland or grassland). Moreover, irrigated croplands had 402 Mg less SIC per hectare than their corresponding rainfed lands (Kim et al., 2020). A field experiment conducted for over 75 years in California showed that the SIC stocks of a 2 m soil profile in irrigated croplands were significantly lower than those in non-irrigated fallow land (Eshel et al., 2007). These SIC losses or SIC accumulation depend on the carbonate content in the irrigation water (Buglio et al., 2016). Moisture increased CO_2 emissions from SIC compared to air dried soil, and the losses were further intensified in acidifying soils (Lardner et al., 2015). Compared to dry soil, the SIC-derived CO_2 emissions from a moist alkaline soil were increased by 23 times and approximately 48 times when the pH decreased by approximately 0.5 and 1 unit, respectively (Lardner et al., 2015). This implied that in addition to acidification, alterations in the soil water balance, such as those induced by irrigation,

Table 1
Loss of carbonate contents due to acidification in some field experiments.

Vegetation	Duration (years)	Acidification source	N Input ($\text{kg ha}^{-1} \text{ yr}^{-1}$)	pH Decrease (units)	Carbonate Loss (%)	Reference
Wheat	101	N fertilizer	96	2.50	5	Bolton (1972)
Wheat-maize	20	N fertilizer	276	1.0	3.1	Heimann et al. (2015)
Wheat-Maize	22	N fertilizer	353	0.23	3.2	Zhang et al. (2016)
Rice-Wheat	25	N fertilizer	285	1.70	0.6	Zhang et al. (2017)
Grassland	20	N deposition	–	0.64	62	Yang et al. (2012)
Wheat	12	N fertilizer	240	0.22	29	Jin et al. (2018)
Maize	22	N fertilizer	165	2.0	55	Qiu et al. (2016)
Maize	25	N fertilizer	212	1.6	74	Wang et al. (2020)
Rice	25	N fertilizer	184	1.1	44 ^a	Wang et al. (2020)
Wheat	10	N fertilizer	152	–	10 ^a	Moreno et al. (2006)
Grassland	40	N, S deposition	–	0.14	0.4	Zhang et al. (2021)
Grassland	40	N, S deposition	–	0.16	5	Zhang et al. (2021)
Shrub Encroachment	1	Landuse change	–	0.17	18.8	Liu et al. (2020)

^aLoss represents the % carbonate-C removed after 25 years of N fertilization compared to 5 years.

could also increase the dissolution and losses of SIC, and could alter its stocks within decades.

4.2. Soil inorganic C losses and CO₂ emissions from liming of acidic soils

Soil acidification is a widespread global phenomenon, and acidity requires periodic neutralization to achieve and sustain higher productivity. The application of lime is the most widely practiced and effective method to ameliorate soil acidity (Goulding, 2016). Approximately 3.8 billion hectares of acidic soils receive limestone or dolomite at 1 Mg ha⁻¹ annually (Chmiel et al., 2016). Thus, approximately 30 Mt and 2.5 Mt of lime are annually applied to agricultural soils in the USA

Table 2
Addition of lime in acidic soils and its contribution to CO₂ emissions.

Experiment	Soil Type/ Texture	Original Soil pH	CaCO ₃ addition	Lime- derived CO ₂ emissions	Reference
			Mg ha ⁻¹	(%)	
Field	Peatland	4.87–5.29	7.8	12–19 [#]	Biasi et al. (2008)
Incubation	Clay	4.76	4.6	108–112 ^{\$}	Bramble et al. (2021)
Incubation	Loam	4.82	4.6	39–74 ^{\$}	Bramble et al. (2021)
Field	Loamy skeletal	5.6	2.0	21.66 ^{\$}	Cho et al. (2019)
Incubation	Silt	7.64	50	26 [#]	Bertrand et al. (2007)
Incubation	Silt loam	4.8–5.4	4.4–17.6	35–93 [¶]	Fuentes et al. (2006)
Growth chamber	Sandy clay loam	4.11	2.04	64–188 [¶]	Ahmad et al. (2013)
Incubation	Very fine	4.43	4	1.6–32 [¶]	Bramble et al. (2019)
Incubation	Clayey	4.52	4	16.8–78 [¶]	Bramble et al. (2019)
Field	Acidic cambisol	3.2	30	31 [¶]	Brumme & Beese (1992)
Incubation	Andisol	5.2	6.0	77 [#]	Dumale et al. (2011)
Incubation	Ultisol	4.2	4.8	66 [#]	Dumale et al. (2011)
			g kg ⁻¹ soil	(%)	
Incubation	Loam	6.8–7.7	2–630	30 [#]	Tamir et al. (2011)
Incubation	Loam	7.6	144.7	13 [#]	Stevenson and Verburg, 2006
Incubation	Udric Cambisols	4.21	50	0.9 ^{\$}	Xiao et al. (2018)
Incubation	Leptosol	6.56	50	0.8 ^{\$}	Feng et al. (2016)
Growth chamber	Chromic Luvisol	4.11	1.2	11 [#]	Ahmad et al. (2020)
Incubation	Chromic Luvisol	4.11	4.6–9.2	17–32 [#]	Ahmad et al. (2014)
Laboratory	Peatland	4.87–5.29	0*	53–70 [#]	Biasi et al. (2008)
Incubation	Arenosol	4.69	0.2–0.5	28–82 ^{\$}	Grover et al. (2017)
Incubation	Luvisol	4.56	0.7–1.8	74–85 ^{\$}	Grover et al. (2017)
Incubation	Luvisolic silt loam	7.26–7.55	–	62–80 [#]	Ramnarine et al. (2012)

Lime was added only in the field experiment, and later the same soil was used in the incubation experiment without any further liming. ^{} relative change in total CO₂ emissions with lime. [#] contribution of lime- or carbonate-derived CO₂ to total CO₂ emissions. ^{\$} percentage of the quantity of C from lime released as CO₂.

and Australia, respectively (ABS, 2003; West and McBride, 2005). Lime use and its annual application rates are considerably increasing because of the continuous increase in soil acidity and area of acidic soils. In some soils without lime addition, the pH decreases to a level that does not support crop growth.

In addition to neutralizing acidification, lime also directly influences the C and N cycles and GHG fluxes (Kunhikrishnan et al., 2016). Lime addition accelerates CO₂ emissions through the dissolution of carbonates in lime (Equation 3; Biasi et al., 2008; Ahmad et al., 2013). According to the Intergovernmental Panel on Climate Change (IPCC), all the carbonates in lime are released as CO₂ within the first year of application (Eggleston et al., 2006). This assumption has been challenged and it was observed that carbonate losses may actually occur in 2–3 years; therefore, countries have been permitted to report their own emission factors (West and McBride, 2005; De Klein et al., 2006; Ahmad et al., 2014). In fact, the CO₂ generated via liming ranges between 5.3% and 100% of lime applied in field and laboratory experiments (Table 2; Page et al., 2010; Ahmad et al., 2014; Kunhikrishnan et al., 2016; Bramble et al., 2021). The application of lime in Australia caused a loss of approximately 1.0 Tg of CO₂ in 2002 (Page et al., 2010). The United States Environmental Protection Agency estimated that 9 Tg of CO₂ was emitted from approximately 20 Tg of lime applied in 2001 (West and McBride, 2005). Similarly, net CO₂ emissions from liming of agricultural soils in Brazil during 1990–2000 were estimated at approximately 7.2 Tg CO₂ yr⁻¹ (Bernoux et al., 2003). At the global scale, CO₂ release from the liming of acidic soils is considerably higher (273 Tg C yr⁻¹) than that from the dissolution of indigenous carbonates in calcareous soils because of N fertilization-induced acidification (7.5 Tg C yr⁻¹) (Zamanian et al., 2018). Furthermore, these losses are estimated to reach 820 Tg C yr⁻¹ by 2050 (Zamanian et al., 2021).

Apart from the direct contribution of lime to CO₂ emissions, liming accelerates various processes resulting in CO₂ production, such as: 1) increasing microbial activity and mineralization of SOM, litter, and rhizodeposits (Ahmad et al., 2014); 2) increase in plant root activity causing increased respiration (Hinsinger et al., 2003); and 3) increase in the number and activity of earthworms, which accelerates soil particle mixing, bacterial dissemination, and litter decomposition (Kreutzer, 1995). Moreover, CO₂ emissions occur from the fossil fuels used to extract, crush, deliver, and spread lime in agricultural fields. West and Marland (2002) estimated that the production and transport of crushed limestone to agricultural fields caused CO₂ emissions of approximately 36 kg C Mg⁻¹ of limestone. In addition, consumption of fossil fuel during lime application or spreading is expected to release approximately 12 kg C ha⁻¹ (West and Marland, 2002). Assuming a minimum application rate of 5 Mg ha⁻¹ of crushed rocks every 5 years, a loss of approximately 38 kg C ha⁻¹ yr⁻¹ is expected from the production, transport, and application of lime. Considering a three-fold increase in lime application worldwide by 2050 (Tilman et al., 2001), the contribution of lime to CO₂ emissions and subsequent climate change and global warming could be highly significant.

In summary, carbonate-containing and lime-receiving soils are causing substantial losses of inorganic C as CO₂, estimated at approximately 0.3 Gt C for 2018, which is approximately equivalent to 30% of the CO₂ emissions due to land-use changes (Zamanian et al., 2018). Even a small enhancement in acidity could further intensify these losses, strongly jeopardizing global efforts to increase C sequestration and mitigate climate change. This demonstrated that SIC losses at such a large scale significantly affect the C budgets of regional and global terrestrial ecosystems. Moreover, large SIC stocks in calcareous soils lead to continual CO₂ losses for centuries via acid neutralization under continuous N fertilization. Therefore, acidification-induced SIC losses and CO₂ emissions should not be neglected, but incorporated into regional and global C budgets and models (Yang et al., 2012). It is not possible to accurately predict global C flux or develop effective climate change mitigation strategies without an improved understanding of SIC cycling (Rey, 2015).

Liming may also increase C sequestration. Liming facilitates better plant growth, which results in a higher C input to soils (Paradelo et al., 2015). It may also lead to the redistribution of SOC from labile to more stable and humified pools due to strong base cation bonding between organic compounds with charged mineral surfaces (Manna et al., 2007; Rowley et al., 2018). These processes were confirmed by a 129-years long-term experiment at Rothamsted, which showed that limed plots have 2–20 times higher SOC sequestration than non-limed plots (Fornera et al., 2011).

5. SIC losses and the global climate change

Climate change factors such as rising temperature, increasing atmospheric CO₂ level, and increased periods of drought highly influence all biotic and abiotic processes involved in soil C transformations. The effects of these factors on the dynamics, sequestration, and loss of SOC have been extensively studied. However, their effects on SIC transformations have received little attention.

Global warming may increase surface temperature by up to 4.8 °C in the 21st century based on various model projections (IPCC et al., 2013; Richardson et al., 2018; Fernández-Martínez et al., 2019). All processes causing acidification were strongly affected by climate change factors, which directly influenced SIC dynamics and losses (Fig. 4). The nitrification process, which is the main route of acidification in croplands, was highly intensified at high temperatures. Increased temperatures increase the activity and abundance of ammonia-oxidizing archaea communities that enhance nitrification (Hu et al., 2016; Nguyen et al., 2019). A meta-analysis showed that high temperatures increased the net soil nitrification rate by 32.2% at the global scale and by 56% on the Tibetan Plateau (Bai et al., 2013; Zhang et al., 2015). Another meta-analysis reported that high temperatures reduced soil microbial biomass N and intensified N mineralization (Dai et al., 2020). Simultaneously, increased mineralization due to warming provides more NH₄⁺ substrates for nitrification and causes acidification (Butler et al., 2012; Bai et al., 2013). Therefore, a combination of increasing temperature, increasing N fertilization, and faster nitrification intensifies soil acidification and subsequent SIC dissolution and losses.

The solubility of CaCO₃ in pure water at 25 °C is relatively low (0.013 g L⁻¹) (Aylward, 2007), but increases by 30 times in CO₂-saturated water (approximately 0.3 g L⁻¹) (Zamanian et al., 2018). Increasing atmospheric CO₂ concentrations lead to increased plant biomass, higher organism activity, and respiration (Ferdush and Paul,

2021). This adds increased amounts of CO₂ to the soil water, which, along with high temperature, causes more CaCO₃ dissolution and losses (Fig. 4; Ahmad et al., 2014). The contribution of SIC to total soil CO₂ emissions ranges from 10 to 40% (Inglima et al., 2009) up to 70% at high temperatures (Chevallier et al., 2017). Moreover, Ahmad et al. (2014) reported that an increase in the incubation temperature from 20 °C to 40 °C intensified the release of CO₂ from lime by 59%.

6. Are SIC losses irrecoverable?

Irrecoverable SIC losses are defined as the fraction that is irreversibly released into the atmosphere (Goldstein et al., 2020). Transformation of SOC to atmospheric CO₂ occurs cyclically, and SOC contents could be increased through effective management practices (Fig. 5). However, the direct conversion pathway of atmospheric CO₂ to SIC is unreliable and currently debated. Soil inorganic C losses by neutralization of N-fertilization-induced acidification are generally irrecoverable within the human lifetime scale. This is because Ca²⁺ and Mg²⁺ are released during carbonate dissolution, which are lost with nitrate (Equation 3) to maintain the charge balance (Fig. 4). Other cations, except Ca²⁺ and Mg²⁺, cannot trap the CO₂ released by root respiration and microbial decomposition of organic matter to form carbonates (Zamanian et al., 2021).

Fertilizers such as single super phosphate, triple super phosphate, and calcium ammonium nitrate can be sources of Ca²⁺ input in soils, but their application rate has continuously decreased with time (Fig. 6; Raza et al., 2021). Lower Ca²⁺ input hinders carbonate formation in soils which confirmed that C losses from SIC are largely irrecoverable. Zamanian et al. (2021) estimated the irrecoverable losses of SIC and reported that approximately 0.41 Gt C has been released as CO₂ to the atmosphere from agricultural soils during the past five decades, and an additional 0.72 Gt C would be lost until 2050. These irrecoverable losses could have long-term effects on soil structure, nutrient availability, microbial activity, and subsequent effects on plant and soil productivity.

7. Consequences of carbonate losses on soil-plant-water systems

7.1. Soil health and aggregate stability

CaCO₃ depletion is detrimental to soil health and ecosystem services (Rowley et al., 2020), because it is crucial for several functions related to

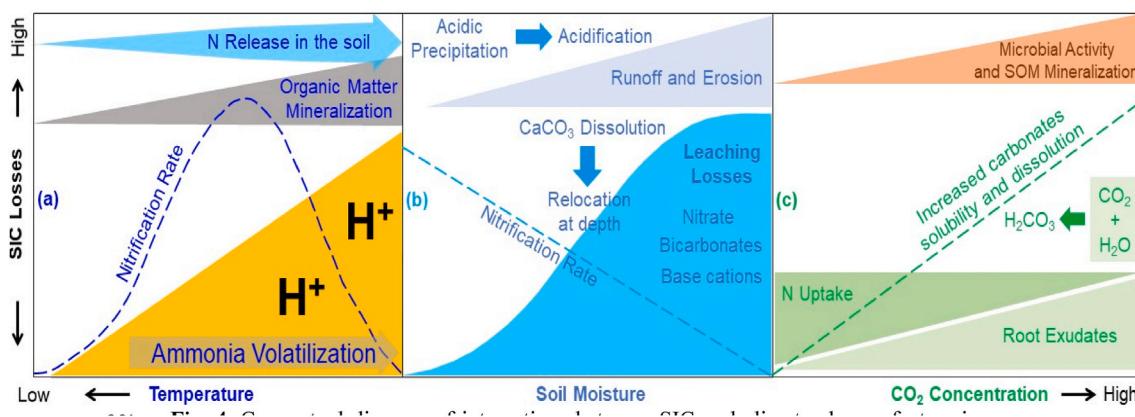


Fig. 4. Conceptual diagram of interactions between SIC and climate change factors i.e. temperature (a), moisture (b), and CO₂ concentration (c). Rise in temperature accelerates nitrification rates and input of H⁺ ions. It also increases H⁺ input from ammonia volatilization, and mineralization of organic matter. Increase in moisture facilitates carbonate dissolution and can cause acidification if base cations are leached. High rainfall intensity also increases carbonate losses with runoff and erosion. Nitrification process is inhibited with rise in moisture and plants by up taking more NH₄⁺ release more H⁺. Increase in CO₂ concentration in the soil with moisture facilitates formation of carbonic acid, which causes acidification. Nitrogen assimilation usually become low with increase in CO₂ concentration and results in N losses and acidification. Root exudates are increased at higher CO₂ concentration which usually end up in organic acids. Root exudates also increase microbial activity and accelerate organic matter mineralization. All processes and fluxes driving SIC losses are increased with increase in the intensity of climate change factors.

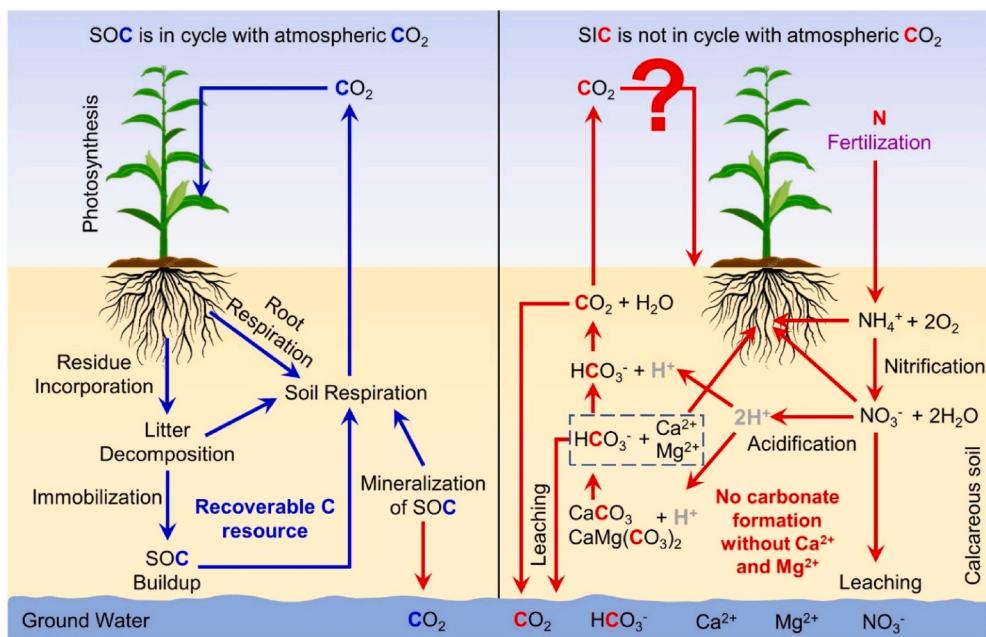


Fig. 5. Changes in soil organic carbon (SOC) and soil inorganic carbon (SIC) in calcareous soil. In contrast to SOC, SIC does not occur in cycle with atmospheric CO_2 over the human life timescale and when the Ca^{2+} (and Mg^{2+}) are lost, the C in the form of carbonates is irrecoverable.

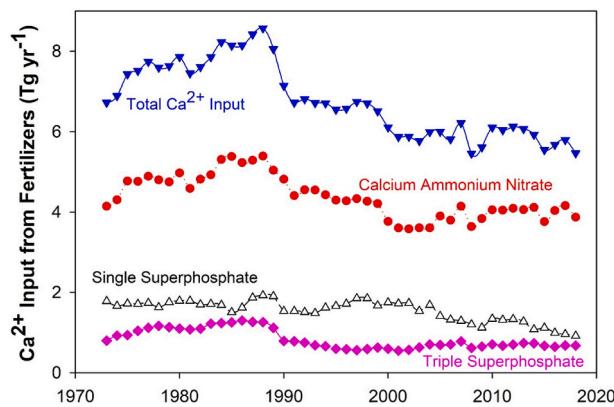


Fig. 6. Global Ca^{2+} input to croplands through fertilizers. Most commonly used calcium-containing fertilizers are calcium ammonium nitrate (18.5% Ca^{2+} , red), single super phosphate (17% Ca^{2+} , black), and triple super phosphate (16% Ca^{2+} , pink). Ca^{2+} input to croplands increased from 3.2 to 8.6 Tg yr^{-1} during 1961–1988, and has been continuously decreasing since 1988 due to the decline in application of all calcium-containing fertilizers.

pedogenic, chemical, (micro)biological, and rhizosphere processes (Fig. 7). For example, CaCO_3 losses can decrease aggregate stability, resulting in the formation of weak-structured soils with poor aeration and water permeability, and high bulk density (Fernández-Ugalde et al., 2014), which increases the soil sensitivity to loss by erosion. Carbonates also act as physical barriers to SOM loss via aggregation and cementing. Furthermore, the formation of Ca^{2+} -OM complexes renders SOM stable and resistant to decomposition (Rowley et al., 2018).

7.2. Nutrient availability and plant growth

Soil inorganic C loss resulting from acidification and higher water availability leads to the loss of base cations from the soil, causing Ca^{2+} and Mg^{2+} deficiencies (Chen et al., 2013). Acidification-induced Ca^{2+} and Mg^{2+} deficiencies in soil are increasing worldwide. Notably, the deficiency of Ca^{2+} is a major cause of severe yield reduction or crop failure in many countries, particularly in southern China (Lucas et al.,

2011; Schroder et al., 2011). The N fixation capacity of legumes is significantly reduced in carbonate-free soils at pH values below 6 (Vassileva et al., 1997; Ferguson et al., 2013). Ca^{2+} is important for legume growth and nodulation (Watkin et al., 1997). Moreover, soil acidity limits rhizobium survival and persistence, deteriorates the symbiotic relationship between rhizobia and legumes, and inhibits nitrogenase activity (Ferguson et al., 2013).

Carbonate-free soils exhibit increased bioavailability and mobility of heavy metals, aluminum, and manganese (Bian et al., 2013; Bai et al., 2015). At pH values below 4.5, when the buffers of Fe and Al oxides are active (Equations 6 and 7), the concentrations of free Al^{3+} , Fe^{3+} , and Mn^{2+} are toxic to plants (Van Den Berg et al., 2005; Bowman et al., 2008). The grains of winter wheat grown in carbonate-free soils of the Yangtze River Delta had twice the Cd and thrice the Ni than wheat grains harvested from carbonate-containing soils (Wang et al., 2015). Similarly, higher Cd concentrations were found in Swiss chard and lettuce cultivated in acidic soils with pH approximately 4.8–5.7, than in calcareous soils with pH ranging 7.4–7.8 (Mahler et al., 1978). Zhu et al. (2018) estimated that N fertilization will cause a decrease of 1.1–2.5 units in soil pH, and 13.2% of the total croplands will be affected by Al^{3+} toxicity by 2050 if soil acidification rates are not decreased.

Abundance of Al^{3+} and certain plant nutrients (Mn^{2+} and Fe^{3+}), and deficiency of Ca^{2+} , Mg^{2+} , and K^{+} considerably offset the nutritional balance, which severely reduces the yield, quality, and root growth of crops (Lucas et al., 2011; Schroder et al., 2011; Goulding, 2016). Yield losses of over 50% have been attributed to low pH for a wide range of crop species, including both legume and non-legume varieties (Ferguson et al., 2013). Zhu et al. (2020) reported on the basis of the yield-pH relationship that cereal yields in China decreased by 4% during 1980–2010 due to an increase in soil acidification. Furthermore, yield reduction would increase by up to 24% by 2050 if N fertilization-induced acidification continually increases at the same rate. Therefore, carbonate losses from soils not only decrease the soil pH but also influences many processes that consequently affect food production, food quality, and soil health.

7.3. Riverine alkalinity and oceanic acidification

Carbonate dissolution causes release of bicarbonates and base

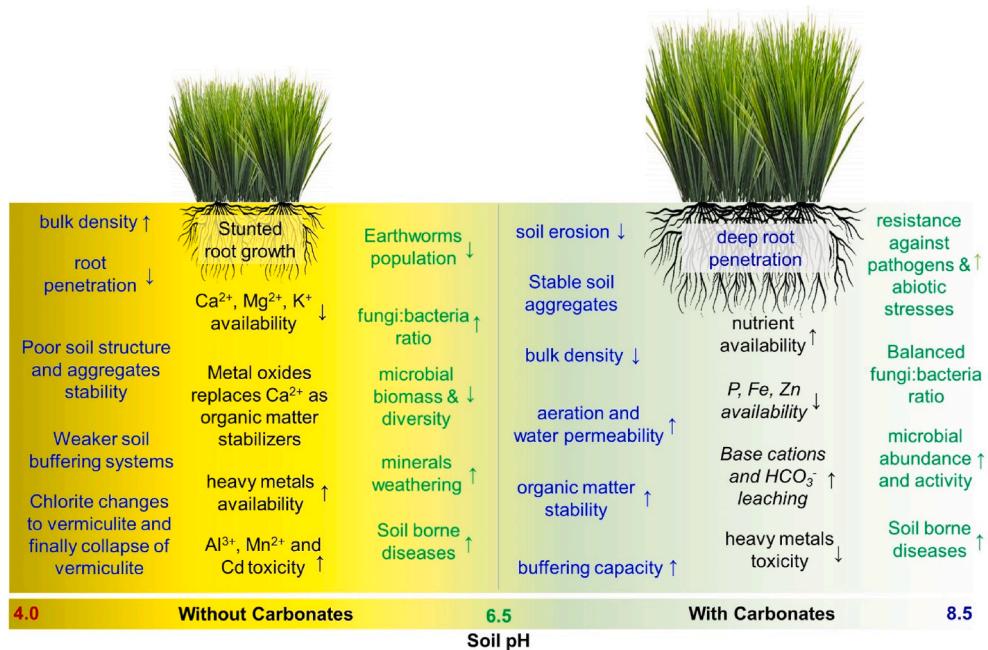


Fig. 7. Differences in physical (blue), chemical (black), and biological (green) properties of soils with and without carbonates and their effects on plant growth and development. The intensity of the yellow color on the left shows intensified acidification. The italicized text on the right indicates negative effects of carbonate.

cations, which when introduced into groundwater, freshwater, lakes, and rivers can cause localized alkalinization and water hardness, and degrade its quality for consumption by most living organisms (Kaushal et al., 2018). The bicarbonate released into surface water may either remain as HCO₃⁻ and sequester CO₂, or react with H⁺ ions to release CO₂ (Drever, 1988). A decrease in the water pH (<6.0) and an increase in the water temperature facilitate the release of CO₂ from HCO₃⁻ (Drever, 1988). The concentration of dissolved CO₂ in surface water is generally higher than that in the atmosphere. Therefore, the CO₂ dissolution capacity is reduced; hence, many rivers and lakes worldwide act as a net CO₂ source (Telmer and Veizer, 1999; Zhai et al., 2007; Rasera et al., 2008; Page et al., 2010). The Yangtze River in China, the Guadalquivir Estuary River in Spain, and the St Lawrence River in North America are estimated to lose 2–4.6%, 34%, and 30%, respectively, of the dissolved inorganic C they annually transport as HCO₃⁻ (Telmer and Veizer, 1999; de la Paz et al., 2010; Zhai et al., 2007). In oceans, HCO₃⁻ can react with Ca²⁺ to form CaCO₃ and lead to precipitation (Page et al., 2010).

The increasing atmospheric CO₂ levels (partly from SIC) are absorbed by oceans causing a decrease in pH, which modifies the chemical speciation of surface, coastal, and estuarine waters, as well as the physiology and population dynamics of aquatic organisms (Doney et al., 2020). For example, ocean acidification causes shifts in seawater carbonate chemistry towards higher CaCO₃ solubility, and thus decreases CaCO₃ saturation, which directly influences the shell formation of marine organisms (Doney et al., 2009). The shells of young Dungeness crabs along the US West Coast were dissolving because of a lower pH level, because of the acidification of the Pacific Ocean (Bednaršek et al., 2020). Coral reefs have high biological diversity and provide various ecosystem services to numerous species, and their framework is dependent on the presence of CaCO₃ (Eyre et al., 2014). Ocean acidification and global warming owing to intensified CaCO₃ dissolution are expected to cause a high loss risk of most (70%–90%) coral-dominated ecosystems (Allen et al., 2018).

8. Strategies to manage soil acidification

8.1. Pros and cons of liming in managing soil acidification

Liming is one of the most effective methods to neutralize acidity, but if not appropriately managed, it could have several disadvantages in terms of environmental pollution. For example, NH₃ volatilization losses from soils are intensified by an increase in pH. Lime application increased NH₃ volatilization by 3.3 kg ha⁻¹ for each 0.1 unit of increase in pH (Smith et al., 2009). Excessive lime addition and subsequent increase in soil pH can increase the molybdenum content to toxic levels and decrease the availability of nutrients, such as P, Mg, K, Zn, Cu, and B, which reduces plant growth (Filipek, 2011). Liming also increases the rates of SOM decomposition, mineralization, and nitrification, which act as precursors of N and C losses (Paradelo et al., 2015; Grover et al., 2017). Finally, the application of high rates of lime to highly weathered tropical soils is often detrimental to soil structure, and to the availability of phosphorus and several micronutrients, particularly zinc.

In addition to the above effects and risks of liming, lime availability and application are not universally feasible. For example, subsurface acidity is difficult to remediate because of the lower solubility and slow movement of neutralizing substances, such as lime and base-rich organic matter (Tang et al., 2013; Butterly et al., 2020). Liming also increased production costs, because farmers have to incur transportation charges and high labor and monetary costs. Notably, the lime resources were not distributed uniformly, their availability and supply were limited, and a gradual decrease in the stocks in some regions might further increase the transportation cost. Therefore, complementary, alternative, innovative, long-term, and sustainable methods to control soil acidification are necessary.

8.2. Efficient and balanced nitrogen fertilization

Over-application of N fertilizers should be avoided. Optimizing N fertilization could reduce the amount of H⁺ ions released into soils. Improving NUE and increasing the N acquisition capacity of crops are direct methods to reduce acidification. The following N management practices are recommended to decrease acidification: (i) optimum

application of N fertilizer based on soil tests, (ii) deep placement of fertilizer, (iii) minimum N application as a base dose, and (iv) N addition in multiple stages to enhance NUE and decrease its losses. The use of ammonium-based fertilizers should be reduced and substituted with nitrate-based fertilizers, which have comparatively low acidification potential regardless of the high price. Judicious and balanced N fertilization should be practiced considering the crop demand and residual N in the soil. For example, nitrification and urease inhibitors, which decrease H⁺ release by hindering nitrification, can be incorporated with N fertilizers, reducing N losses and improving NUE (Raza et al., 2019). The use of nano-enabled N fertilizer could be another promising strategy to decrease acidification, even though research on this aspect is lacking. Nano-enabled N fertilizers have a high sorption capacity and a higher surface-to-volume ratio, and are released very slowly in comparison to conventional fertilizers (Kotegoda et al., 2017). This approach improved the NUE and decreased N loss and leaching into groundwater.

8.3. Use of crop residues, manure, and biochar

Recycling of crop residues and the addition of animal manure decreased soil acidification, but increased CO₂ emissions. Manure application can reduce soil acidification and cause short-term pH increase through: (i) addition of base cations back to the soil (Cai et al., 2015), (ii) decarboxylation of organic anions (Xiao et al., 2013; Dippold et al., 2014), (iii) ammonification of labile organic N in manure (Xu et al., 2006), and (iv) formation of Al-organic matter complexes (Hagvall et al., 2015). Notably, crop residues and manure also release N into the soil, which can cause acidification (Chen et al., 2014). Biochar addition can induce a liming effect in soils because it contains a large amount of alkaline ash (Dai et al., 2017; Ghorbani et al., 2021), and therefore decreases acidification (Dai et al., 2017; Shi et al., 2019).

8.4. Acid-tolerant genotypes

Development of acid-tolerant cultivars is also a promising alternative to liming and other acid-neutralizing practices. Acid-tolerant genotypes release organic ligands from their roots which form complexes with Al³⁺ and protect plants from the adverse effects of lower pH (Kochian et al., 2015).

In summary, sustainable agricultural practices involving the recycling of plant residues to the soil and the use of N fertilizer in combination with manure or efficiency-enhanced fertilizers could significantly reduce acidification risks.

9. Future outlook and recommendations

The global human population is expected to exceed 9 billion by 2050. Most cereals, fruits, and vegetables grow best in neutral soils, and therefore, the future of food production is at risk under the prevailing conditions of increasing N fertilization and soil acidification. Thus, the consequences of N fertilization-induced acidification should be considered from a larger perspective at the ecosystem level in terms of food security and safety, disruption of the global C cycle, and its contribution to climate change and global warming.

In agroecosystems, in addition to N mineralization, there are several processes that cause acidification (Fig. 1); however, information about the acidification potential of all such processes is relatively low. Most field and modeling studies have only focused on the acidification induced by N fertilizers. Future studies should focus on quantifying the total H⁺ budget by considering the contributions from all processes presented in Fig. 1. Soil acidification and its effects on SIC dissolution remains poorly understood and underestimated when the total H⁺ budget is not considered.

The effects of climate change on SOC dynamics have been extensively studied, but cannot provide a comprehensive representation of the soil C cycle without determining the effects of SIC. Information

about the sensitivity of SIC towards climate change factors is lacking, and research in this aspect should be prioritized to accurately estimate C fluxes in a changing climate.

Finally, studying SIC dynamics requires further research, owing to several unanswered questions: 1) What fraction of SIC dissolution by acidification is lost as CO₂? 2) What fraction is lost as HCO₃⁻ via leaching? 3) How are SOC stocks affected by changes in SIC stocks under N-induced acidification? 4) What are the management strategies for sequestering atmospheric C as SIC? 5) How can SIC loss be reduced by increasing NUE with nitrification inhibitors, nano-fertilizers, or other strategies, or by stabilizing base cations with biochar application? Determining the answers to these questions would help develop methodologies to accurately quantify the contribution of SIC to the global C cycle.

10. Conclusions

A global increase in N fertilization provides an opportunity to increase C sequestration as soil organic C (SOC). However, the consequences of fertilization-induced acidification, which is occurring worldwide, and the depletion of soil inorganic C (SIC) stocks have been ignored till date. SIC-originated CO₂ emissions owing to acidity neutralization in calcareous and limed soils are very high, which can offset the benefits of C sequestration as SOC. Furthermore, SIC losses deteriorate soil health, decrease plant productivity, increase heavy metal availability, and consequently threaten global food security and human health. Therefore, existing C budget schemes and models should include SIC dynamics to provide an accurate and comprehensive representation of the C cycle, which would help formulate relevant policies and control measures. Acidification and the associated SIC losses could be reduced by optimizing N fertilization, increasing NUE, and using manure. Quantifying the acidification-related SIC losses under variable land-use systems and climate change scenarios and exploring the possibilities of capturing atmospheric CO₂ as SIC are important future research avenues.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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