

Nitrogen fertilization raises CO₂ efflux from inorganic carbon: A global assessment

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Abstract

Nitrogen (N) fertilization is an indispensable agricultural practice worldwide, serving the survival of half of the global population. Nitrogen transformation (e.g., nitrification) in soil as well as plant N uptake releases protons and increases soil acidification. Neutralizing this acidity in carbonate-containing soils (7.49×10^9 ha; ca. 54% of the global land surface area) leads to a CO₂ release corresponding to 0.21 kg C per kg of applied N. We here for the first time raise this problem of acidification of carbonate-containing soils and assess the global CO₂ release from pedogenic and geogenic carbonates in the upper 1 m soil depth. Based on a global N-fertilization map and the distribution of soils containing CaCO₃, we calculated the CO₂ amount released annually from the acidification of such soils to be 7.48×10^{12} g C/year. This level of continuous CO₂ release will remain constant at least until soils are fertilized by N. Moreover, we estimated that about 273×10^{12} g CO₂-C are released annually in the same process of CaCO₃ neutralization but involving liming of acid soils. These two CO₂ sources correspond to 3% of global CO₂ emissions by fossil fuel combustion or 30% of CO₂ by land-use changes. Importantly, the duration of CO₂ release after land-use changes usually lasts only 1–3 decades before a new C equilibrium is reached in soil. In contrast, the CO₂ released by CaCO₃ acidification cannot reach equilibrium, as long as N fertilizer is applied until it becomes completely neutralized. As the CaCO₃ amounts in soils, if present, are nearly unlimited, their complete dissolution and CO₂ release will take centuries or even millennia. This emphasizes the necessity of preventing soil acidification in N-fertilized soils as an effective strategy to inhibit millennia of CO₂ efflux to the atmosphere. Hence, N fertilization should be strictly calculated based on plant-demand, and overfertilization should be avoided not only because N is a source of local and regional eutrophication, but also because of the continuous CO₂ release by global acidification.

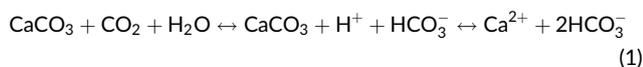
KEYWORDS

CO₂ efflux, global acidification assessment, global warming, mitigation policy, nitrogen fertilization, soil acidification mechanisms, soil inorganic carbon

1 | INTRODUCTION

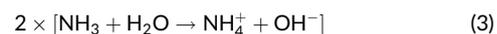
Soils with about 6,000 Peta gram (10^{15} g) carbon (C) down to 3 m depth contain the largest terrestrial C stock (Le Quéré et al., 2016). Changes of CO_2 efflux from soils directly affect atmospheric CO_2 and subsequently global warming. Carbon is stored in soils in two main forms: organic and inorganic (Eswaran et al., 2000), and CO_2 efflux from soils originates from these two C sources. The agricultural sector is one of the main sources of atmospheric CO_2 (Lal, 2004; Tongwane et al., 2016). Agricultural management practices, such as tillage and fertilization, control the decomposition rates of soil organic matter (SOM) (Lal, 2004; Marquina et al., 2015; Sauerbeck, 2001; West & Marland, 2002), strongly influencing the CO_2 exchange between soil and atmosphere. Fertilization rate and type (Lal, 2004) also affect soil CO_2 efflux by controlling the quality and quantity of SOM (Khorramdel, Koocheki, Nassiri Mahallati, Khorasani, & Ghorbani, 2013) and thus its decomposition rate (Sauerbeck, 2001). While soil inorganic carbon (SIC) comprises most of the soil C pool, especially in arid and semiarid regions (Eswaran et al., 2000), the contribution of CaCO_3 to soil CO_2 efflux is usually neglected (Kuzyakov, 2006; Rey, 2015; Zamanian, Pustovoytov, & Kuzyakov, 2016). This is because (1) calcareous soils are mostly distributed in arid and semiarid regions, where water deficiency merely leads to redistribution of CaCO_3 in the soil profile (Zamanian et al., 2016). (2) Most CaCO_3 stocks are located in subsoil (Díaz-Hernández, Fernández, & González, 2003; Wang, Li, Ye, Chu, & Wang, 2010), which decreases the exchange of CaCO_3 -C with atmospheric CO_2 . The SIC is also generally disregarded as a C stock compared to SOC because (1) SOC is closely connected with soil fertility and crop productivity, and (2) in contrast to SOC, SIC cannot be efficiently managed using organic fertilizers, crop rotation, and tillage practices.

CO_2 efflux from CaCO_3 naturally takes place through CaCO_3 dissolution in weak acids i.e., H_2CO_3 , produced by roots and microbial respiration Equation (1) (Sanderman, 2012; Zamanian et al., 2016). The CaCO_3 solubility is relatively low (0.013 g/L in pure H_2O at 25°C (Aylward, 2007), but increases by a factor of about 30 (~0.3 g/L) in CO_2 -saturated water) and consumes the root and microbially respired CO_2 Equation (1). Therefore, CaCO_3 dissolution leads to CO_2 uptake (Equation (1) is shifted to the right), but only as long as C remains in the aqueous phase as HCO_3^- (Beaulieu, Goddérís, Donnadieu, Labat, & Roelandt, 2012; Monger et al., 2015). Increasing temperature and evapotranspiration as well as direct CO_2 discharge from streams cause CO_2 release into the atmosphere (Wallin et al., 2013) — the Equation (1) becomes shifted to the left. Thus, the processes described by Equation (1) are CO_2 neutral.



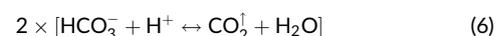
In agroecosystems, the CaCO_3 dissolution rate increases by up to one order of magnitude after organic and mineral fertilization, especially nitrogen (N) fertilizers — mostly urea, $\text{CO}(\text{NH}_2)_2$ (Chao, Changli, Junkun, Yun, & Hongbing, 2011; Rice & Herman, 2012)

Equations (2–6). Urea hydrolyzes to ammonium by microbially produced urease Equations (2 and 3). Thereafter, nitrifying bacteria oxidize ammonium to nitrate, release H^+ , and thus acidify the soil Equation (4) (Bolan, Hedley, & White, 1991).



In poorly aerated soils, NH_4^+ will be not converted to NO_3^- and will be taken up by roots in exchange for H^+ . Consequently, even in the absence of nitrification, N fertilization produces acidity Equation (4).

In calcareous soils, where various carbonate minerals — mostly CaCO_3 — are the main buffering system (Bloom, Skjellberg, & Sumner, 2005; Huang et al., 2015), the acidity induced via NH_4^+ uptake by plants and nitrification by microorganisms is neutralized through accelerating CaCO_3 dissolution Equation (5 and 6) (Sanderman, 2012).



Dissolution of CaCO_3 via this anthropogenic source of acidity leads to CO_2 efflux Equation (6) (Chen, Wang, Luo, & Ye, 2013; Gandois, Perrin, & Probst, 2011) and loss of CaCO_3 , i.e., Ca^{2+} leaching from the soil profile (Chmiel et al., 2016). For example, 46–95 kg $\text{CaCO}_3 \text{ ha}^{-1} \text{ year}^{-1}$ has been lost following 12 years of application of 100 kg urea-N $\text{ha}^{-1} \text{ year}^{-1}$ (Conyers, Heenan, Poile, Cullis, & Helyar, 1996). Therefore, N fertilization changes the inorganic C stocks in soil (Dalal, Harms, Krull, & Wang, 2005), increases CO_2 efflux to the atmosphere and subsequently affects the world's C cycle and global warming (Drever & Stillings, 1997; Huang et al., 2015). This is the direct effect of N fertilization on CO_2 release from SIC.

In noncalcareous soils, in the absence of CaCO_3 , the cations on the exchange sites of soil organic matter and clays (Bar-Yosef, Rosenberg, Kafkafi, & Sposito, 1988; Bloom et al., 2005) buffer the acidity produced by nitrification. Substitution of exchangeable cations with protons and their release in solution (Frank & Stuanes, 2003; Nohrstedt, Jacobson, & Sikström, 2000) cause the leaching of base cations, e.g., Ca^{2+} , at a rate of 0.45 mol m^2/year from the soil profile (Gandois et al., 2011) and thus promote soil acidification.

The acidification due to N fertilization depends on the type and amount of applied N fertilizer and plants' N-use efficiencies. The global average N fertilization exceeds 80 kg N $\text{ha}^{-1} \text{ year}^{-1}$ to achieve optimal crop yields. N-fertilizer consumption is expected to increase at a rate of ca. 1% per year up to 2030 (FAO, 2000), following the increase in the human population and in food demand (Rice & Herman, 2012). The estimated N-use efficiency is between 25% and

65% (<50% on average) (Zhang et al., 2004). This means that more than 50% of the applied urea is lost from agricultural fields through leaching as NO_3^- and/or volatilization by denitrification (Smil, 2002). This leached fraction as NO_3^- , however, adds huge amounts of protons to the soil (Barak, Jobe, Krueger, Peterson, & Laird, 1997; Bolan et al., 1991). Note also that N-use efficiencies below 10% have been reported in regional scales (Guo et al., 2010), leading to an additional N loss and even greater soil acidification.

The acidity produced by N fertilization can be 25 times higher than that induced by acid rain (Vries & Breeuwsma, 1987). Hence, soil pH may decline significantly – 0.13–0.8 units –after only a few decades of N fertilization (Guo et al., 2010; Mahler, Wilson, Shafii, & Price, 2016); the rate is more than 0.03 unit pH per year (Conyers et al., 1996). Due to these effects of N fertilization on soil pH, and especially the CO_2 efflux from CaCO_3 and the subsequent effects on the C cycle and global warming, this study (1) estimates the contribution of soil CaCO_3 to CO_2 efflux by N fertilization-induced acidification, (2) predicts the regions vulnerable to acidification following CaCO_3 depletion due to excessive N fertilization, and (3) assesses the CO_2 efflux by liming of acidic soils.

2 | MATERIALS AND METHODS

To quantify the contribution of N fertilizers to CO_2 efflux due to CaCO_3 dissolution Equations (2-6), the following information was collected: (1) the global distribution of application rates of N

fertilizers, and (2) the global distribution of inorganic C in soil. The global application rate of N fertilizers was obtained from the data presented in (Potter, Ramankutty, Bennett, & Donner, 2010) (Figure 1).

These data are provided in raster GeoTIFF formats with a raster grid cell size of 0.5 degrees in latitude and longitude at “<http://sedac.ciesin.columbia.edu/data/set/ferman-v1-nitrogen-fertilizer-application>”.

The global distribution of soil CaCO_3 was obtained from a soil inorganic C map (USDA-NRCS, 2000) (Figure 2). The map shows the distribution of CaCO_3 as kilograms C per hectare and refers to the inorganic C content for a depth of one meter.

For further quantifications, five assumptions were made. (1) The total N added to the soils (N fertilizer map, Figure 1) is in the form of urea, which is the most common N fertilizer used globally (Chao et al., 2011; Rice & Herman, 2012). (2) Ammonium volatilization is negligible (in irrigated corn it has been reported as 6.6% (Halvorson, Del Grosso, & Stewart, 2016), but usually less than 5% of N fertilizers is volatilized to the atmosphere (Butterbach-Bahl, Baggs, Dannenmann, Kiese, & Zechmeister-Boltenstern, 2013) and at least similar or even higher N amounts are deposited on the soil surface due to wet and dry deposition). (3) Denitrification is negligible because it takes place (i) mainly in soils with oxygen limitation, which are rare in the semiarid and arid areas where calcareous soils are mostly distributed or (ii) in irrigated calcareous soils, whose area, however, is small. (4) As long as CaCO_3 with 20,000 mmol_e/kg buffering capacity is present in the soil, the

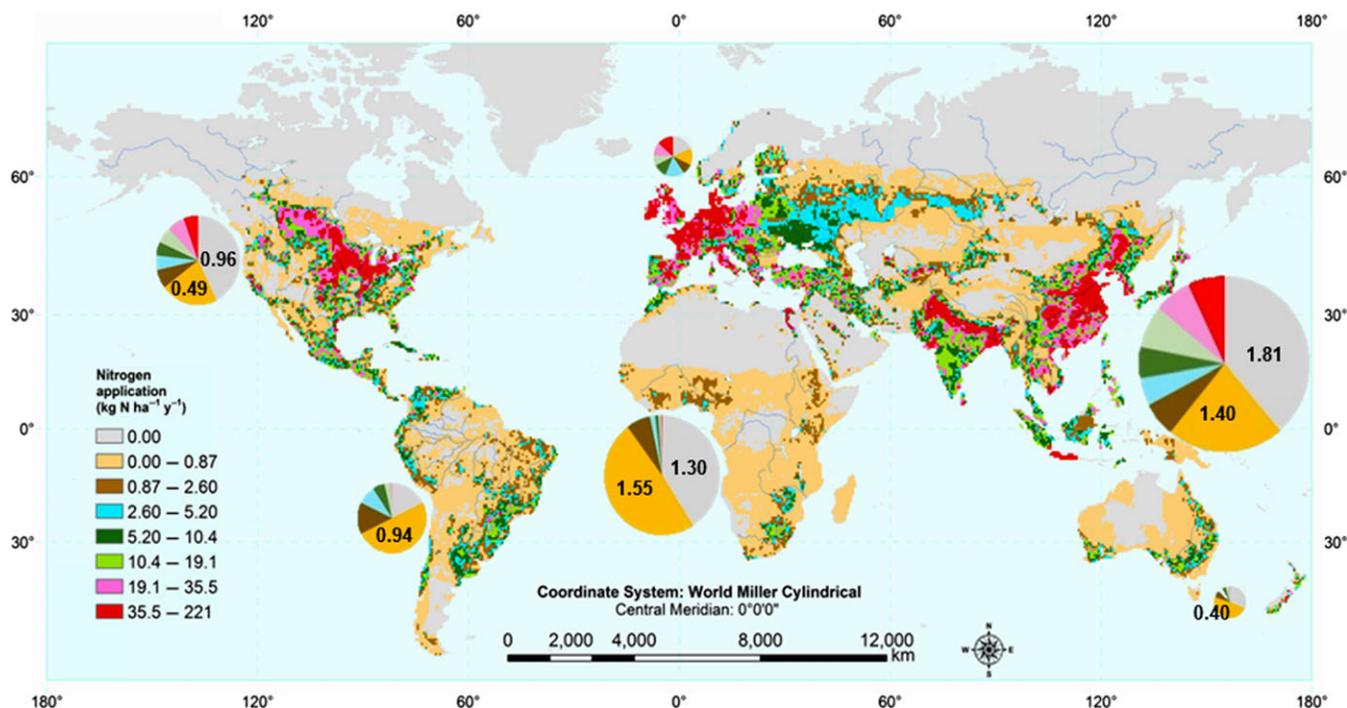


FIGURE 1 World map of applied nitrogen fertilizers (modified from Potter et al., 2010). The global application rate of N fertilizers is presented as kilogram N per hectare per year. The size of the inset pie graphs corresponds to the total surface area ($\times 10^9$ ha) of applied N fertilization and individual N-fertilization classes (corresponding to the N application scale on the bottom left) for the continents North and Central America, South America, Europe, Africa, Asia, and Oceania. The numbers on the pie graphs reflect the surface area ($\times 10^9$ ha) of the main N-fertilization classes

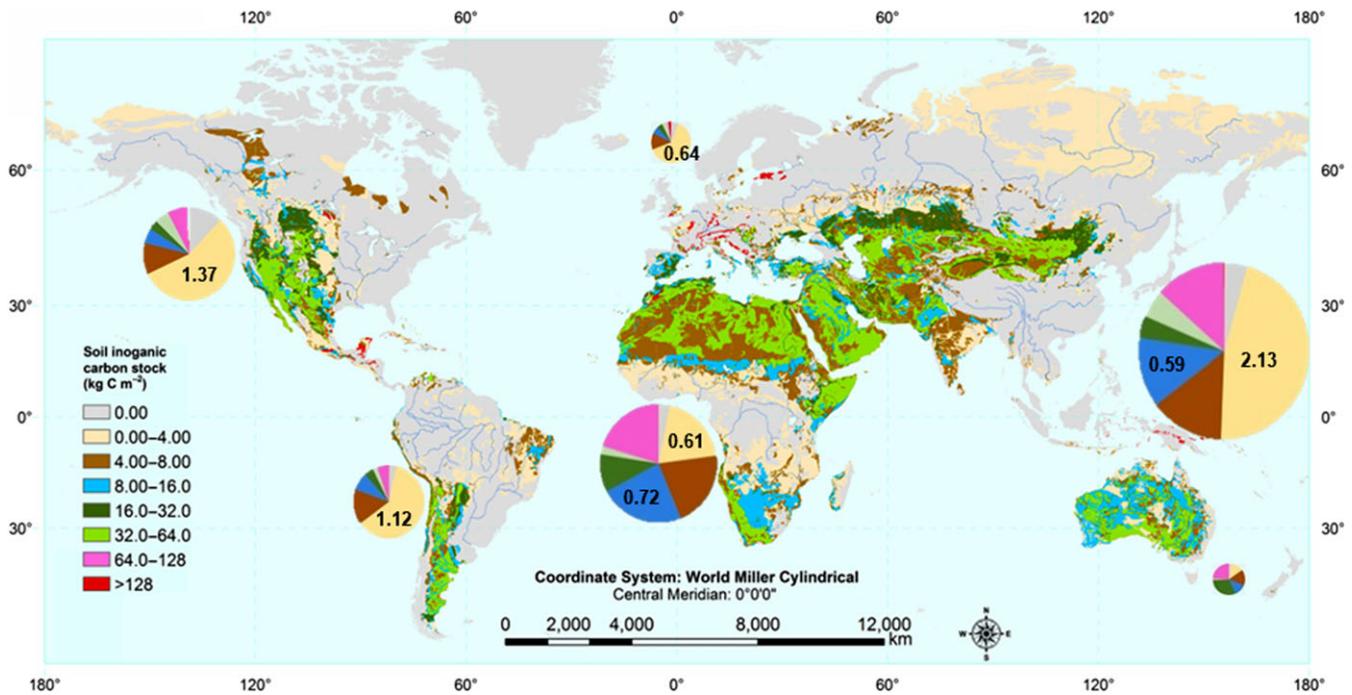


FIGURE 2 World map of soil inorganic carbon (SIC) stocks, i.e., CaCO_3 (USDA-NRCS, 2000). Note that SIC stocks are presented as kilogram C per square meter down to a depth of one meter. The inset pie graphs show the surface area ($\times 10^9$ ha) of each class for the continents North and Central America, South America, Europe, Africa, Asia, and Oceania. The numbers on the pie graphs reflect the surface area ($\times 10^9$ ha) of the main SIC classes (scale in bottom left corner)

exchangeable cations on the exchange sites of soil organic matter (1,880 mmol_c/kg of SOM at $\text{pH} = 7.5$) and of the soil clay fraction (6–8 mmol_c/kg at $\text{pH} = 6$) (Bloom et al., 2005) are of minor importance and can be neglected. Finally, (5) the main source of uncertainty in the calculated CO_2 efflux from CaCO_3 by neutralization of N fertilization-induced acidity is the accuracy of the estimated CaCO_3 content (Figure 2). Here, the precise data about the amount of N fertilization, types of N fertilizers and N-use efficiencies at smaller scales, e.g., regions, reduce this uncertainty.

Based on these assumptions and according to Equations (2–6), theoretically one mole urea (60 g) will neutralize 1 mole CaCO_3 (100 g). Based on 50% N-use efficiency, however, only half of the applied N undergoes hydrolysis and releases protons to neutralize CaCO_3 . Therefore, 1 mole of applied urea in soil neutralizes 0.5 mole CaCO_3 (Zhang et al., 2004). This calculation suggests that applying one kg N will dissolve 1.78 kg CaCO_3 , which in turn produces 0.78 kg CO_2 or 0.21 kg $\text{CO}_2\text{-C}$ for each kg of N. N-use efficiency, however, differs in various countries and ranges from about 65% in USA to 30% in India and 25% in China (Zhang et al., 2015). Therefore, applying one kg N in those countries will produce 0.15, 0.30, and 0.32 kg $\text{CO}_2\text{-C}$, respectively, due to CaCO_3 dissolution.

Data were analyzed in ArcMap 10.3. Both maps (Figures 1 and 2) were first georeferenced. A mask was prepared from the CaCO_3 map representing the regions containing inorganic C. In this mask, the pixel values of regions with inorganic C were set to one and the rest to zero. Then, a map showing CO_2 efflux was prepared following Equation (7):

$$\text{CO}_2 \text{ efflux (kg C ha}^{-1}\text{)} = \text{mask} \times \text{map of N application (kg N ha}^{-1}\text{)} \times \text{conversion factor} \quad (7)$$

Conversion factors are 0.32 for China, 0.30 for India, 0.15 for USA and West Europe, and 0.21 for the rest of the world.

To calculate the total CO_2 efflux (kg C), we multiplied the map of CO_2 efflux (kg C/ha) with its grid size and then summed the values up globally.

In addition to CO_2 efflux due to CaCO_3 dissolution, applying N fertilizers could result in soil acidification in the absence of CaCO_3 . We prepared a map showing the risk of acidification based on the regions where CaCO_3 is absent in the soil. To this end, two masks were prepared from the maps of CaCO_3 and N application rate. The first mask (Mask1) represents the soils without CaCO_3 . In this mask, the pixel values of regions without CaCO_3 were set to one and the rest to zero. The second mask (Mask2) represents the regions where N fertilizers are applied. In this mask, the pixel values of regions with N fertilization were set to one and the rest to zero. Then, a map showing the acidification risk was prepared by overlapping these two masks.

3 | RESULTS

The total soil CO_2 efflux due to CaCO_3 dissolution following N fertilization was calculated as 7.48×10^{12} g C/year (Table 1).

The areas with the highest CO_2 efflux induced by N fertilization are located in central USA, northern France and the Iberian

TABLE 1 The contribution of CaCO_3 dissolution to CO_2 efflux from soil after nitrogen fertilization based on the applied N-fertilization classes and the respective surface area (only soils containing CaCO_3 considered)

Applied N ($\text{kg N ha}^{-1} \text{ year}^{-1}$)	Surface area (10^9 ha)	CO_2 efflux (10^{12} g C/year)
0.44	2.85	0.26
1.74	0.61	0.21
3.90	0.42	0.33
7.80	0.35	0.56
14.7	0.32	0.95
27.3	0.28	1.44
128	0.26	3.73
	5.09	7.48

Peninsula, eastern China, northern India along the Ganges River, and along the Nile River in Egypt (Figure 3).

The combined area of the mentioned regions ($0.26 \times 10^9 \text{ ha}$) comprises only 5.13% of the total surface area ($5.09 \times 10^9 \text{ ha}$) emitting CO_2 induced by N fertilization (Table 1), but their contribution to fertilization-induced CO_2 efflux is almost 50%. These areas are also among those vulnerable to acidification (Figure 4). The total area of soils under acidification risk is estimated at about $2.04 \times 10^9 \text{ ha}$, which represents somewhat more than half of the already acidified soils ($3.79 \times 10^9 \text{ ha}$) worldwide (Figure 4).

The next step was to calculate the CO_2 efflux via agricultural lime dissolution. We calculated CO_2 efflux via agricultural lime dissolution based on the following assumptions: (1) the estimated surface

area of acidified soils is $3.79 \times 10^9 \text{ ha}$ (Figure 4), (2) the average annual application of lime is 1 ton per hectare (Chmiel et al., 2016) and (3) ca. 60% of the applied lime will be released as CO_2 to the atmosphere (West & McBride, 2005). The remaining 40% may leach out from the soil, reach the oceans and precipitate again as CaCO_3 . Accordingly, we calculated that the CO_2 efflux from agricultural lime dissolution is $273 \times 10^{12} \text{ g C/year}$.

4 | DISCUSSION

The total contribution of CaCO_3 dissolution to CO_2 efflux from soil due to N fertilization was calculated to be $7.48 \times 10^{12} \text{ g C/year}$ ($27.4 \times 10^{12} \text{ g CO}_2/\text{year}$) (Table 1). This falls into the upper range of the previous estimation ($3.24\text{--}7.91 \times 10^{12} \text{ g C/year}$) (Perrin, Probst, & Probst, 2008). Perrin et al. (2008) generalized the measured acidity induced by N fertilization in a catchment in France to the whole world. France, however, is among the countries with the highest N-use efficiency (about 65%, Zhang et al., 2015) and thus the lowest acidity induced by N fertilization compared with other countries such as China and India, with average N-use efficiencies of 25% and 30%, respectively (Zhang et al., 2015). Hence, the much lower N-use efficiency in most regions of the world, along with the higher surface area of such regions compared with France, explains the higher estimation of CO_2 emission due to N fertilization (Table 1). Importantly, this significant CO_2 flux (Perrin et al., 2008) is a continuous process that can last not only for decades but probably for centuries and longer. This is because of (1) the very high CaCO_3 stocks in soil (695–748 Pg C down to 1 m depth (Batjes, 1996) and

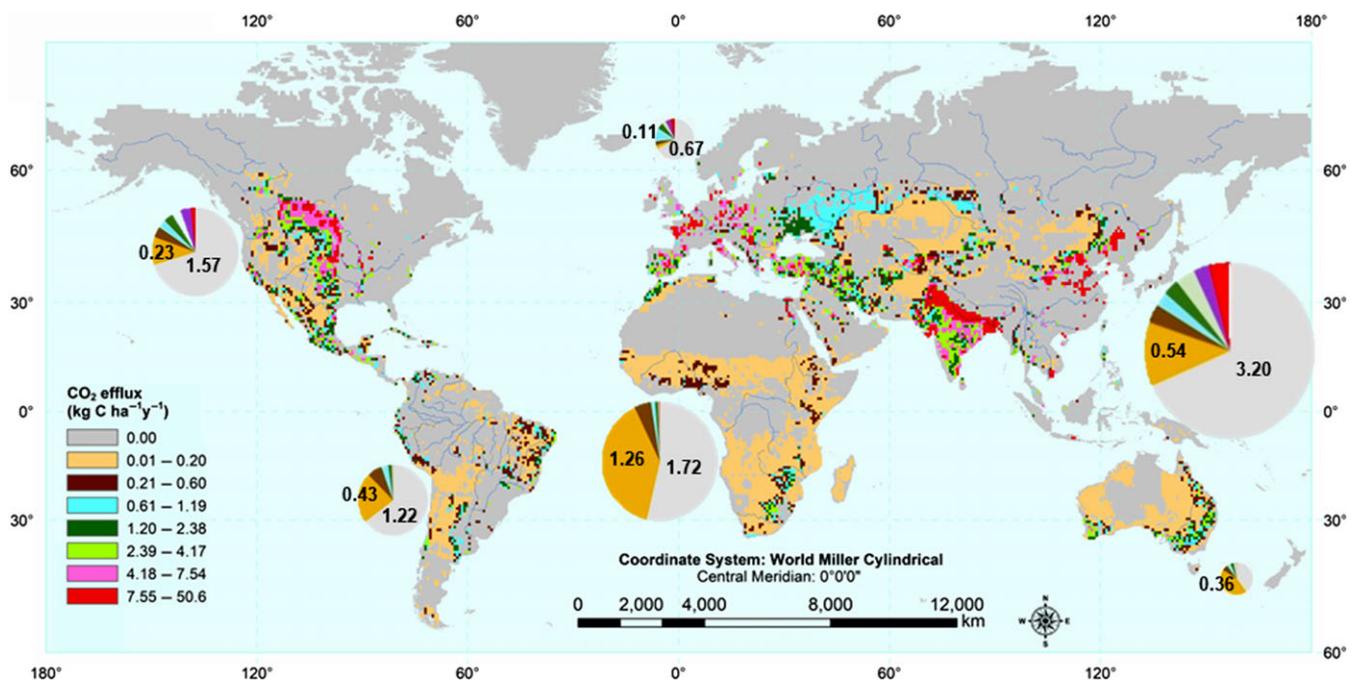


FIGURE 3 Map of CO_2 efflux intensity from soil via CaCO_3 dissolution due to nitrogen fertilization. The inset pie graphs show the surface area ($\times 10^9 \text{ ha}$) of each CO_2 efflux class for the continent North and Central America, South America, Europe, Africa, Asia, and Oceania. The numbers on the pie graphs reflect the surface area ($\times 10^9 \text{ ha}$) of the main CO_2 efflux classes (scale in bottom left corner)

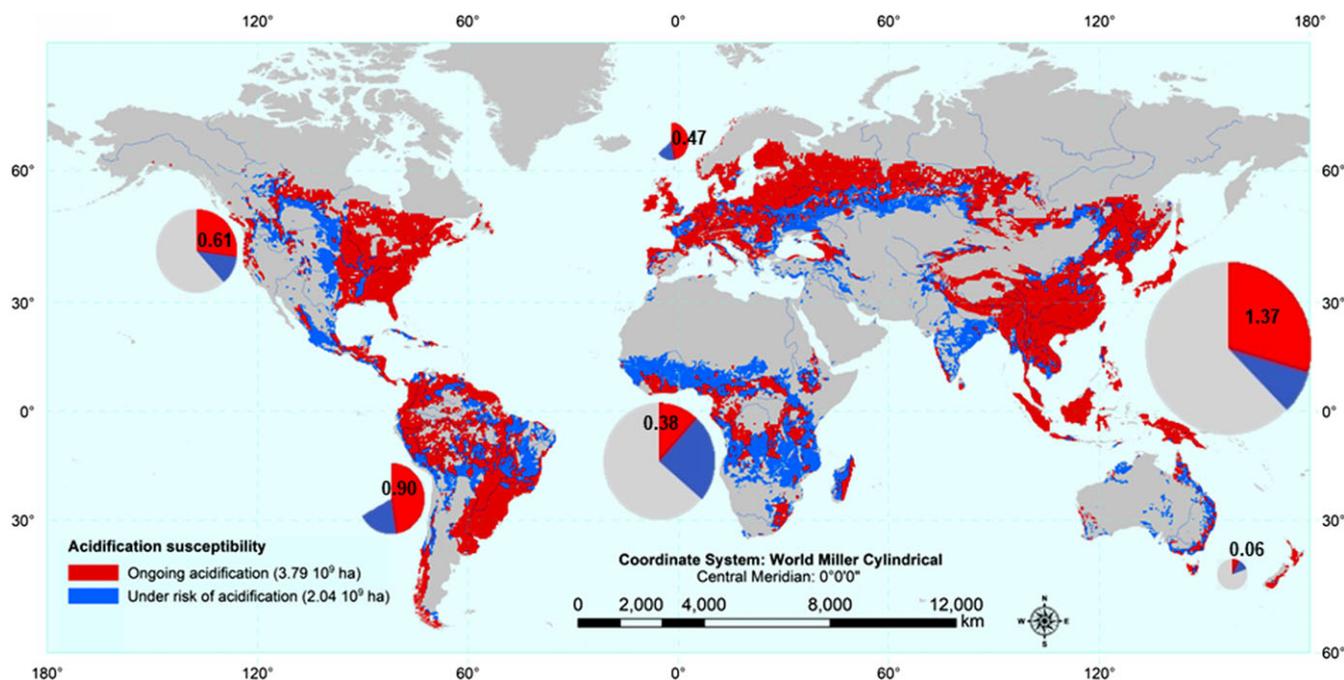


FIGURE 4 Map of soil acidification due to N fertilization. Red areas: ongoing acidification, i.e., N fertilization in carbonate-free soils. Blue areas: soils highly susceptible to acidification, i.e., areas with the lowest CaCO_3 content ($<4 \text{ kg C m}^{-2}$) in Fig. 2. The inset pie graphs show the surface area ($\times 10^9 \text{ ha}$) of soils that are acidified or under acidification risk for each continent (North and Central America, South America, Europe, Africa, Asia, and Oceania). The numbers on the red pie graphs reflect the surface area ($\times 10^9 \text{ ha}$) of the ongoing acidification. Lime is used in some parts of these areas to neutralize soil acidification and therefore contributes to CO_2 fluxes into the atmosphere

(2) the absence of equilibrium between CaCO_3 production and its dissolution. In contrast, CO_2 efflux from land-use changes is limited to 1–3 decades (Don, Schumacher, & Freibauer, 2011; Guillaume, Holtkamp, Damris, Brummer, & Kuzyakov, 2016; Poeplau et al., 2011). After this period, the new equilibrium between the plant C input, organic C stocks in soil and CO_2 losses is nearly reached and no further CO_2 losses from SOC are expected, at least until new major land-use changes. Furthermore, in contrast to SOC pools with a comparatively short turnover rate of years to decades (Hsieh, 1993; Neff et al., 2002; Zang et al., 2018), the long turnover rate of SIC (ca. 85,000 year – without anthropogenic impact) (Schlesinger, 1985) makes CaCO_3 dissolution due to acidity induced by N fertilization, a unidirectional source of CO_2 efflux during human history. Nonetheless, N fertilization is necessary to maintain sustainable agriculture and secure food production. Accordingly, plant-demand N-fertilization management strategies should be taken to prevent soil acidification and help reduce CO_2 efflux from SIC dissolution. Note also that the global N fertilization in 2018 is anticipated to reach $11.9 \times 10^{10} \text{ kg N}$ (FAO, 2015), i.e., a 1.7-fold increase compared to the $7.09 \times 10^{10} \text{ kg N}$ in 2010 (Potter et al., 2010) considered in our study. Therefore, assuming an equal increase in N fertilization worldwide, the CO_2 efflux from SIC due to N fertilization will boost to $12.7 \times 10^{12} \text{ g C/year}$ ($46.6 \times 10^{12} \text{ g CO}_2/\text{year}$).

Liming of acidified soils, is a usual practice to increase the pH, to improve nutrient availability, and thus to increase crop productivity. Dissolution of lime (mainly CaCO_3) applied on agricultural soils with $\text{pH} < 6.5$ also produces CO_2 . Despite a lack of information about the global amounts of lime added to agricultural soils, its contribution to

the CO_2 efflux has been estimated at about $85 \times 10^{12} \text{ g C/year}$ (based on actual liming rates in the USA) (Suarez, 2000). Suarez (2000) mentioned that if the potential liming demand (i.e., all the limestone needed) was applied, the result in the USA, would be about three times higher. Applying this factor to the global estimation by Suarez (2000) yields $253 \times 10^{12} \text{ g C/year}$. Our estimation ($273 \times 10^{12} \text{ g C/year}$) based on potential liming rates to treat all acid soils (Figure 4), therefore closely agrees with the $253 \times 10^{12} \text{ g C/year}$ suggested by Suarez (2000). This amount corresponds to ca. 3% of the CO_2 efflux from fossil fuel burning (8.3 Pg C/year) or about 30% of the CO_2 from land-use changes (0.9 Pg C/year) (IPCC, 2007). This calls for considering CO_2 efflux from CaCO_3 dissolution in atmospheric CO_2 reduction policies. Improving N-fertilization management to decrease CO_2 efflux from CaCO_3 and prohibiting soil acidification are effective strategies for decision makers to reduce long-term greenhouse gases emissions not only for N_2O – as previously accepted (Dalal, Wang, Robertson, & Parton, 2003; Meng, Ding, & Cai, 2005; Shcherbak, Millar, & Robertson, 2014; Stehfest & Bouwman, 2006) – but also for CO_2 from CaCO_3 dissolution. Furthermore, decalcification of soils by N fertilization also decreases SOM stability, because binding of organic matter on Ca^{2+} is one of the most important mechanisms of C stabilization and sequestration in soils containing CaCO_3 (Rowley, Grand, & Verrecchia, 2018). Therefore, N fertilization will affect CO_2 efflux not only directly – by acidification and release of CO_2 from CaCO_3 – but also indirectly by decreasing SOM stability (and consequently its faster microbial decomposition) by removing Ca^{2+} . This process is important not only in CaCO_3 -containing soils, but also in soils with neutral

or slightly acidic pH, where Ca^{2+} is the dominating cation on exchange sites. Hence, N fertilization should be strictly calculated based on plant-demand and should avoid any overfertilization not only because N is a source of local and regional eutrophication, but also because of the continuous CO_2 release by global acidification.

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