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Nitrogen fertilizers control CO_2 emission from calcareous soils: implications for land management and global warming

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Soil acidification has increasingly become a critical issue for sustainable production due to the excessive nitrogen (N) fertilization in agricultural systems. Application of N fertilizers and the consequent nitrification yield protons (H^+), which strongly and irreversibly accelerate dissolution of soil inorganic carbon (SIC) e.g., $CaCO_3$, leading to CO_2 release in the atmosphere. Here, ^{14}C-labeled $CaCO_3$ was added to calcareous soil (0.75% $CaCO_3$) to investigate the effects of chicken manure, urea, NH_4NO_3, KNO_3 and $(NH_4)_2SO_4$ on soil acidification and to estimate the SIC contribution to CO_2 emission. 250 mL gas-tight jars were filled with a cropland soil (pH = 7.2), homogenously mixed with 1.3% $Ca^{14}CO_3$ powder (^{14}C activity = 11.3 kBq pot^{-1}). Following fertilization in rates of 0.1, 0.15, 0.25 g N kg^{-1} soil, NaOH was applied to trap the emitted CO_2 and to determine ^{14}C activity. $CaCO_3$ addition increased soil pH values by 0.17-0.43 units. Addition of ammonium-based fertilizers ($(NH_4)_2SO_4$, NH_4NO_3) strongly decreased pH up to 0.3 units. All fertilizers increased CO_2 emission (5.1%-180%) compared to the unfertilized soil after 44 days of incubation except KNO_3. SIC-originated CO_2 due to fertilization was ranged from 2.9 to 160 mg C kg^{-1} (1.1% to 48% of total emitted CO_2). Manure and urea had lowest impacts on SIC-driven CO_2 during the first 5 days (2.9-34 mg C kg^{-1}) irrespective of the application rate. Thereafter, the effects of fertilizers on SIC-originated CO_2 increased in the order: urea < manure < KNO_3 < NH_4NO_3 < $(NH_4)_2SO_4$. As nitrification of $(NH_4)_2SO_4$ yields in 4 mol H^+, which neutralizes 2 mol carbonates, it initially caused the highest SIC-originated CO_2 until 9 days. Urea and NH_4NO_3 release by nitrification 2 mol H^+ per mole of fertilizer, but urea initially hydrolyses to NH_4OH, which increases soil pH. So, urea addition had the minimum SIC loss as CO_2 in the first 5 days, but starting from 16th day, CO_2 emission sharply increased and reached to highest values among the fertilizers. Manure increased SIC-originated CO_2 emission from 23rd day of incubation. Gradual and incomplete mineralization of organic N of chicken manure duration 44 days explains the smallest released CO_2 from $CaCO_3$ and slowest acidification in the first 16 days. Furthermore, Ca^{2+} and Mg^{2+} in manure may be precipitated as carbonates, which decrease the SIC share in the emitted CO_2. Generally, the higher the applied fertilizer amounts, the larger was the proportion of CO_2 released from SIC. Both the fertilizer chemistry and the application rate played significant roles in dissolution of carbonates. Summarizing, the correct selection of the type and amount of fertilizers based on soil properties and plant demand is necessary to decrease SIC-originated CO_2 emission to mitigate global warming, and also save various ecosystem

services such as organic matter stability and increase C sequestration.