THE ROLE OF CALCIUM CARBONATE IN CARBON DIOXIDE (CO_2) EMISSIONS FROM SOILS

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Abstract

Calcium carbonate ($CaCO_3$) plays a significant role in the carbon cycle in soil ecosystems. Its presence in soils can influence carbon dioxide (CO_2) release both through chemical processes and indirectly by affecting microbial activity and physicochemical properties of the soil environment. This article reviews the literature on the effect of $CaCO_3$ on CO_2 release under different soil and climatic conditions. The different mechanisms of $CaCO_3$ transformation in soil depending on environmental conditions are discussed. The difficulties in separating the different sources of CO_2 (biological-respiration and chemical) are highlighted. Possible directions for future research on the interaction of $CaCO_3$ with soil microorganisms, vegetation, soil organic matter content and fertilisation were also identified. The conclusions of the review emphasise the need for further integrated research from the consideration of $CaCO_3$ as a possible source of increased soil CO_2 in both laboratory and field studies.

Keywords: *calcium carbonate, soil respiration, liming, fertilisation, calcareous soils*

1. INTRODUCTION

Soil plays a key role in the global carbon cycle, being the largest terrestrial store of organic matter (SOC) and inorganic carbon (SIC) (Naorem et al., 2022). Soils worldwide are estimated to store 1220-1576 Pg of SOC carbon and 700-1700 Pg of SIC in a layer of up to 1 metre, which exceeds the amount of carbon found in the atmosphere and plant biomass combined (Guo et al.2016). Therefore, soil changes, both natural and due to human activities, can significantly affect the carbon dioxide (CO_2) content of the atmosphere and thus the course of climate change. Emissions from agricultural land use and land cover changes are, after fossil fuel emissions, the second largest anthropological source of carbon in the atmosphere (Scharlemann, 2014).

CO_2 emissions from soils can occur through various processes. One of the most important is the respiration of microorganisms and plant roots, which is associated with the decomposition of organic matter. Another, less frequently analysed but equally important process is the chemical release of CO_2 through dissolution of calcium carbonate ($CaCO_3$) (Islam et al., 2023).

Calcium carbonate in soil can originate from natural weathering processes of calcareous parent material such as limestone, chalk, or dolomite. It is also formed during diagenesis, influenced by abiotic precipitation from aqueous solutions (Ahmad et al. 2015, Ferdush J. and Paul V., 2021, Sun et al.,2023). Liming is a well-known and widely used agricultural practice to neutralize the acidic reaction of arable soils (Ahmad et al.,2013).

The presence of $CaCO_3$ influences a number of soil properties, including soil pH, soil structure, buffering capacity, plant nutrient availability, and the activity of soil microorganisms. All of these factors directly or indirectly influence CO_2 emission dynamics (Sun et al.2023).

There are two main mechanisms by which $CaCO_3$ can affect carbon dioxide emissions from soils (Ferdush J. and Paul V., 2021, Sun et al. 2023):

1. Decomposition of calcium carbonate in an acidic environment leading to CO_2 emission as a product of the chemical reaction.
2. Changing the activity of soil microorganisms can increase or inhibit CO_2 emissions.

Although the role of organic matter in CO_2 emissions has been widely documented, the influence of the inorganic fraction, especially the presence of $CaCO_3$, is much less studied and often not considered in CO_2 emissions from soils. In particular, it is important to consider how calcium carbonate content interacts with other environmental factors, such as moisture, temperature, soil type, soil amendments, and soil biological activity (Lal, 2008, Zamanian et al., 2021, Sun et al., 2023).

The aim of this review is to summarize the current knowledge on the impact of $CaCO_3$ on CO_2 emissions from soils, taking into account both chemical and biological processes. The main mechanisms of influence and the environmental factors that determine these processes will be discussed. Attention is also given to factors that make it difficult to clearly assess the influence of $CaCO_3$ on the carbon balance in the soil environment.

2. CHARACTERISTICS OF CALCIUM CARBONATE IN SOIL

Calcium carbonate ($CaCO_3$) is a common mineral found in soils worldwide. Its presence depends primarily on geological and climatic conditions, and human activity, particularly in agriculture. Soils containing significant amounts of carbonates are primarily calcareous soils, arid climate zone soils (aridisols), and soils subjected to agricultural practices such as liming.

2.1. The origin of $CaCO_3$ in soils

Calcium carbonate can be of the following origins (Zamanian et al.,2016):

- geogenic – present in parent rocks (e.g. limestone, marl) and introduced into the soil as a result of weathering processes,
- pedogenic – it can form secondarily in the soil, e.g. in conditions of low rainfall and high evaporation, where calcium carbonate precipitates from calcium bicarbonate present in soil solutions,
- anthropogenic – added to soils as a neutralising agent for the acidic reaction of soils used for agricultural purposes.

3. MECHANISMS DETERMINING THE INFLUENCE OF CACO3 ON CO2 EMISSION FROM SOILS

The effect of calcium carbonate ($CaCO_3$) on carbon dioxide emissions from soils is complex. It can act both as a direct source of CO_2 through chemical reactions and as a modifier of environmental conditions, that affect microbial activity and the rate of organic matter decomposition. Understanding these mechanisms requires consideration of the interaction between mineral, organic and biological components of the soil (Sun et al., 2023).

3.1. Formation of pedogenic calcium carbonate

Pedogenic carbonate is formed as a secondary carbonate from the dissolution of lithogenic carbonate. Naturally occurring calcium carbonate in rocks reacts with carbon dioxide dissolved in water mainly from biological sources or the atmosphere to produce well-soluble calcium bicarbonate,$Ca(HCO_3)_2$, which then migrates with water and precipitates again as calcium carbonate elsewhere (Islam et al. 2023) according to the following reactions 1 and 2 (Birkeland et al., 1999)

$$2CO_2+2H_2O \rightleftarrows 2HCO_3^- +2H^+ \quad (1)$$

$$Ca^{2+}+2HCO_3^- \rightleftarrows CaCO_3+H_2O+CO_2 \quad (2)$$

Reactions 1 and 2 are equilibrium reactions.

Arid regions favour the formation of pedogenic carbonate (PIC). Four conditions are necessary for PIC formation: (Naorem et al. 2022):

- high soil pH (alkaline),
- source of CO_2 in the soil for the production of HCO_3^-,
- large amount of available Ca^{2+}
- optimum soil moisture level.

High soil pH causes the formation of bicarbonate ion HCO_3^-, because the reduction in H^+ content in the soil causes reaction (1) to proceed to the right. Likewise, a decrease in pH or an increase in soil CO_2 content would cause a reaction (2) to shift to the left (Naorem et al. 2022).

Water-soluble calcium bicarbonate present in soil (equation 2), under appropriate environmental conditions, precipitates to form $CaCO_3$ crystals, which cement soil aggregates (Zamanian K. et al., 2021). Carbon dioxide (CO_2) (equation 1) consumed in the carbonate formation process comes primarily from soil respiration, including autotrophic root respiration and heterotrophic microbial respiration. SIC resources may decline over time in acidic soils due to the dissolution of neutral carbonates, whereas an alkaline environment may provide optimal conditions for the formation and accumulation of insoluble carbonates of both calcium and magnesium in the soil (Ahmad et al., 2015).

3.2. Chemical release of CO_2

In the soil, calcium carbonate undergoes a series of chemical reactions shown in equations 3, 4, and 5 (Sun et al., 2023).

$$CaCO_3\,(s) + 2H^+ \rightleftarrows Ca^{2+}\,(aq) + HCO_3^-\,(aq) \quad (3)$$

$$HCO_3^-\,(aq) + H^+ \rightleftarrows H_2CO_3\,(aq) \quad (4)$$

$$H_2CO_3\,(aq) \rightleftarrows H_2O + CO_2\,(g) \quad (5)$$

One of the main direct mechanisms of CO_2 emissions associated with the presence of $CaCO_3$ in the soil is the chemical decomposition process. This involves the decomposition of calcium carbonate under the influence of acidifying chemical agents. The chemical decomposition of carbonate causes CO_2 emissions during the neutralisation process of hydrogen cations formed in the soil. This reaction occurs as a natural process of increasing soil acidity. If carbonates are decomposed by acids, 1 mole of CO_2 is emitted for each mole of carbonate dissolved (Ahmad et al., 2015) according to equation 6.

$$2H^+ + CaCO_3 \rightarrow H_2O + CO_2\uparrow\,(g) \quad (6)$$

It is assumed that the acids present and formed in the soil dissolve 12–38% of carbonates in limed soils, which results from European and North American studies. (Ahmad et al., 2015).

The source of hydrogen ions (H^+) can be from (Ahmad et al., 2013; Lal, 2008; Sun et al., 2023; Tamir et al., 2011; Zamanian et al., 2021,):

- organic acids secreted by plant roots (e.g. citric acid, oxalic acid),
- biological acidity generated by microorganisms (e.g. nitrifying bacteria that oxidize ammonia to nitrates, producing H^+),
- atmospheric pollutants (e.g. nitrogen and sulfur oxides),
- the use of nitrogen fertilizers such as ammonium sulphate or ammonium nitrate.

The equilibrium of chemical reactions (3-5) depends on: (a) the partial pressure of CO_2 in the pore space (Karberg et al., 2005, Zhao et al., 2017), (b) the soil pH and its moisture content and the availability of calcium and magnesium ions (Sun et al. 2023, Dong et al., 2014), and (c) the mass flow of carbonate forms H_2CO_3 and HCO_3^- ions (Cardinael et al. 2020). Biological activity influences these factors and

can thus contribute to CO_2 emissions or promote $CaCO_3$ precipitation by shifting the equilibrium between the different dissolved, gaseous and solid forms of carbonates. (Cardinael et al. 2020).

On the other hand, in naturally acidic soils or those acidified by atmospheric factors (acid rain) or fertilization, the presence of SIC could shift the equilibrium of chemical reactions to the right (according to equation 6), which consequently leads to CO_2 emissions (Ahmad et al., 2015). Therefore,$CaCO_3$ may be a source of CO_2 emissions regardless of biological activity.

CO_2 emissions from this process can be continuous or intermittent. They are sometimes omitted from soil respiration estimates, which can lead to an underestimation of the total soil CO_2 flux.

3.3. Changing pH and microbial activity

$CaCO_3$ neutralises soil acidification by raising soil pH to the optimum level for plant growth, which increases nutrient availability and prevents toxicity from excess Al^{3+} and H^+ ions (Ribeiro et al., 2024). Increased nutrient availability improves plant productivity (Zhang et al. 2022).

Changes in soil pH have a direct effect on the activity and composition of the soil microflora. The microorganisms responsible for organic matter decomposition and aerobic respiration show the greatest activity in a neutral or slightly acidic environment (pH 6-7.5). An acidic soil reaction (pH 4.3-6) has been shown to significantly increase carbonate recrystallization, while decreasing microbial activity (Cailleau et al. 2005; Zhao et al., 2017).

The increase in pH of acidic soil due to liming may improve habitat conditions for microorganisms, which may lead to an increase in their biomass, enzymatic activity and intensification of organic matter mineralization processes (Kemmitt et al., 2006; Ekenler and Tabatabai, 2003).

Most of the published literature indicates that liming increases CO_2 emissions due to the dissolution of carbonates in the soil, while enhancing heterotrophic respiration of soil microorganisms (Tamir et al., 2011, Straathof et al. 2014, Zhang et al., 2022)

Ribeiro (2024), in his study, noted that liming increased the release of CO_2 from acidic soil, but decreased CO_2 from neutral soil.

As a result, a change in pH via $CaCO_3$ can both increase and decrease CO_2 emissions, depending on the soil type, its initial pH and the level of organic matter.

4. FACTORS DETERMINING THE IMPACT OF $CaCO_3$ ON CO_2 EMISSIONS

Among the factors influencing CO_2 emissions from limestone soils are (Ferdush, J. and Paul, V. , 2021):

- soil texture,
- organic matter content (organic carbon),
- soil moisture and temperature,
- application of mineral fertilisers.

4.1. Soil texture

The size distribution and stability of soil aggregates are important indicators of soil quality (Zhao J. 2017). The presence of $CaCO_3$ affects the physical properties of the soil (Xie, 2024, Paradelo et al.2015):

- by improving the structure of soil aggregates (e.g. through cationic Ca^{2+} bridges),
- increases aeration, which can stimulate aerobic mineralization of organic matter and CO_2 emissions,

Carbonates are considered to be one of the most important stabilising factors in aggregate formation (Pihlap et al. 2021). Aggregate formation in calcareous soils occurs in several ways. One confirmed mechanism is the bridging of Ca^{2+} ions between the surfaces of clay particles and organic matter (SOM). This mechanism increases the stability of micro aggregates and facilitates organic-mineral interactions

(Pihlap et al. 2021). In addition, $CaCO_3^-$ mediated cementation of aggregates can occur through the precipitation of carbonates (Meng and Li, 2019; Yates et al., 2017)

The morphology and origin of carbonates can also significantly affect their dissolution and precipitation kinetics (Ahmad et al., 2015; Islam et al. 2024). Carbonates with smaller particle sizes, characterised by a larger surface area and lower density, may exhibit higher dissolution rates (Islam et al. 2024). In addition, soil carbonate reactivity can be influenced by mineralogy and aggregation, with coarse-grained soils favouring dissolution, while clay soils can protect carbonate particles from soil conditions. Clay soils limit the diffusion of acids produced by agricultural practices and allow the formation of soil microenvironments that protect carbonates from soil conditions (Ahmad et al., 2015; Miller et al., 2007). Carbonates of similar size to the clay and fine dust fractions are the most reactive form in soils (Hartwig et al. 1990).

4.2. Soil Organic Matter content

Plant litter, rhizodeposits and microbial biomass are the main sources of the soil organic carbon pool (SOC) (Zamanian et al., 2016, Mouhamad et al., 2020).

SOC mineralization is an important biochemical process that is directly related to CO_2 emissions and maintaining soil quality (Schlesinger and Andrews 2000). The process of organic matter mineralization is often expressed as the mineralization of carbon (C), nitrogen (N), phosphorus (P), and sulfur (S) by microbial action. Soil pH controls mineralization in the soil due to its direct effect on microbial populations and their activity. It also influences the action of extracellular enzymes, which support the microbial transformation of organic substrates. (Neina, 2019). At higher soil pH, the mineralized fraction of C_{org} increases because the bond between organic components and clay particles is broken (Curtin et al. 1998).

Many studies show interactions between calcium ions and SOC. There is a positive correlation between exchangeable Ca^{2+} (Ca_{Exch}) and SOC content (Rowley et al., 2018). Calcium cations (Ca^{2+}) released from $CaCO_3$ can form stable bonds with humic acids and polysaccharides present in the soil, leading to the formation of soil aggregates and stabilisation of SOM (Erktan et al. 2017, Xie,2024, Stimmler et al. 2024).

It is widely accepted that the presence of $CaCO_3$ positively affects soil structure and creates favorable conditions for SOC stabilization through occlusion, inclusion, or adsorption (Rowley et al., 2018). Enriching soil with Ca^{2+} ion sources, such as lime, may negatively affect SOC mineralization and increase SOC stabilization in soil aggregates. (Camille et al., 2024).

4.3. Water and temperature conditions

Calcareous soils contain pools of both organic and inorganic carbon. The mineralization of organic carbon and the dissolution of inorganic carbon are related to soil moisture. (Dong et al., 2014). Soil moisture influences CO_2 emissions by increasing biological activity in the decomposition of organic matter. (Lellei-Kovács et al., 2011). This may contribute to the formation of bicarbonate ions and carbonate reprecipitation (SIC) according to Equation 1 (Monger et al., 2015). CO_2 emitted from SOC degradation can also form carbonic acid, which interferes with the dissolution of SIC (Cardinael et al., 2020).

Dumale (2011) reported an increase in CO_2 released from lime during the first 24 hours after liming from soil with high field moisture (an increase from 2% emission at 30% field moisture to 6.5% at 70% field moisture). This difference decreased from day 12 after liming..

In a study by Dong (2014), the effect of $CaCO_3$ addition on CO_2 emissions varied as a function of soil moisture and calcium carbonate content. CO_2 emissions from soil increased with increasing soil moisture and $CaCO_3$ content. When the soil moisture content was 70 and 100% of the maximum water capacity (WHC), CO_2 emissions were higher in the $CaCO_3$ - enriched soil than in the unenriched soil. Furthermore, CO_2 production increased with increasing $CaCO_3$ content.

Also, temperature influences CO_2 emissions from calcareous soils. In his study, Hamdi (2011) investigated the dependence of CO_2 emissions from calcareous soils on ambient temperature (20°C,

30°C, 40°C and 50°C). CO_2 emissions increased with temperature. The contribution of CO_2 from carbonates to these emissions appeared to be stimulated by temperature.

4.4. Fertilization

Soil acidification is one of the main global threats to the sustainability of ecosystems, as a change in soil pH can affect the dynamics of SOC and SIC transformations resulting in a loss of inorganic carbon from topsoil layers (Kim et al., 2020). The use of fertilizers, including nitrogen fertilizers, may affect soil acidification. (Raza et al., 2020, Blake et al., 1999).

The rate of acidification of soils fertilized with nitrogen fertilizers is 25 times faster than the natural processes occurring in the environment (Huang et al., 2015, Tao et al. 2024). A decrease in soil pH promotes the dissolution of calcium carbonate and leads to low calcium content in the soil (Tao et al. 2024). Acidification is highly dependent on the type of nitrogen fertiliser (Jia et al., 2022).

The nitrification mechanism is shown below (Havlin et al. 2017):

1. Oxidation of ammonia to nitrites:

Bacteria such as Nitrosomonas oxidize ammonia (NH_4^+) to nitrite (NO_2^-). The chemical equation for this step is:

$$2NH_4^+ + 3\ O_2 \rightarrow 2NO_2^- + 2\ H_2O + 4H^+ \quad (7)$$

2. Oxidation of nitrites to nitrates:

Bacteria such as Nitrobacter oxidize nitrite (NO_2^-) to nitrate (NO_3^-). The chemical equation for this step is:

$$2NO_2^- + O_2 \rightarrow 2NO_3^-. \quad (8)$$

In the nitrification process, hydrogen ions are produced, which leads to the acidification of the soil environment, which can generally be described as:

$$(NH_4)_2SO_4 + 4O_2 \rightleftarrows 4H^+ + 2NO_3^- + SO_4^{2-} + 2H_2O \quad (9)$$

$$NH_4NO_3 + 2O_2 \rightleftarrows 2H^+ + 2NO_3^- + H_2O \quad (10)$$

When applied to soil, urea is hydrolysed by the enzyme urease to NH_4^+ , which is assimilated by plants. This process releases ammonium nitrogen (NH_4^+), which can be taken up by plants, but also leads to potential nitrogen losses in the form of ammonia (NH_3) escaping into the atmosphere.

The decomposition of urea in soil occurs in two stages (Havlin et al. 2017):

1. Urea hydrolysis

Urea $CO(NH_2)_2$ reacts with water (H_2O) in the presence of the enzyme urease to form ammonium carbonate $(NH_4)_2CO_3$.

$$CO(NH_2)_2 + H^+ + 2H_2O \rightleftarrows 2NH_4 + + HCO_3^- \quad (11)$$

2. Release of ammonia and carbon dioxide:

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O \quad (12)$$

Ammonia can be (Havlin et al. 2017):

- Taken up by plants in ammonium form (NH_4^+), if the soil is acidic or neutral.
- Converted into nitrates (NO_3^-) through nitrification. The process occurs in the presence of oxygen and nitrifying bacteria. This leads to soil acidification, as described above.
- Ammonia can be released into the atmosphere as gaseous ammonia (NH_3), which represents a loss of nitrogen from the soil.

General equation for the chemical reaction of urea transformation in soil (Zamanian et al., 2018):

$$CO(NH_2)_2 + 3H_2O \rightleftarrows 2OH^- + 2NH_4^+ + CO_2 \quad (13)$$

In soil acidified by nitrogen fertilisers, an irreversible reaction occurs, leading to the release of CO_2 into the atmosphere (Zamanian et al., 2018, Tao et al., 2024)

$$CaCO_3 + 2H^+ + 2NO_3^- \rightarrow Ca^{2+} + 2NO_3^- + CO_2\uparrow \quad (14)$$

Inorganic soil carbon is non-recoverable because, after the Ca^{2+} and Mg^{2+} ions are leached out along with the accompanying nitrate ion (V) ions NO_3^- (equation 14), there are no other cations in the soil that could capture the carbon dioxide released by the roots during respiration and the microbial decomposition of organic matter (Zamanian et al., 2021).

Approximately 0.8 Gt of carbon is emitted into the atmosphere annually as a result of land use change. (Goldstein et al., 2020).

Intensive removal of soil carbonates due to the use of nitrogen fertilizers deteriorates the soil structure, reduces the stability of organic matter, which leads to the depletion of organic carbon resources (Rowley et al., 2020, Zamanian et al., 2018). Adding organic fertilizers reduces CO_2 emissions from SIC by creating soil aggregates and preventing SIC loss, which allows carbon sequestration in the soil to be maintained (Tao et al. 2024).

5. THE IMPORTANCE OF CALCIUM CARBONATE IN AGRICULTURAL PRACTICES

Soil acidification is one of the main factors limiting agricultural productivity and biological activity in soil ecosystems. Its causes include natural processes (e.g. leaching of base cations) and human activity, including intensive nitrogen fertilisation (Goulding et al., 2016). Low pH limits the bioavailability of nutrients and disrupts the microbiological processes responsible for organic matter cycling (Rousk et al., 2009).

Liming is currently the only practical and accepted solution that effectively prevents soil acidification (Ahmad et al., 2013a, Zamanian et al., 2021). This process involves the use of calcium compounds such as calcium carbonate $CaCO_3$, calcium hydroxide, calcium oxide or, less commonly, dolomite (Paradelo et al., 2015). This is the most commonly used agricultural practice for improving soil pH. An increase in pH improves the habitat conditions for microorganisms, which can lead to an increase in their biomass, enzymatic activity and intensification of organic matter mineralisation processes (Kemmitt et al., 2006; Ekenler & Tabatabai, 2003, Zhang et al. 2022). Liming can also affect the carbon balance in the soil (Kazem Zamanian, 2021). As a result, liming, although agronomically beneficial, may carry a potential risk of increasing CO_2 emissions (Zhang et al. 2022), especially with the simultaneous use of acidifying fertilizers (e.g. ammonium nitrates). Based on a meta-analysis, Zhang (2022) found that liming increased soil CO_2 emissions by 41%. In his research, Ahmad (2013a) found that the daily rate of mineralization and decomposition of total carbon and soil-derived carbon increased significantly with the addition of lime. An increase in incubation temperature from 20 to 40°C also accelerated the decomposition of CO2–C derived from lime. This may lead to a rapid depletion of inorganic carbon in the topsoil layers (Kim et al. 2020).

6. SOIL RESPIRATION

One of the main indicators of soil microbial activity is soil respiration. Measuring the respiratory activity of soil organisms, known as the basal respiration rate (RESP), is one of the most commonly performed soil microbiological analyses. Respiration activity is a measure of the rate of organic matter decomposition and carbon cycling in the soil system. (Schlesinger, W. H., Andrews, J. A.,2000)

This soil respiration process involves two main sources (Kuzyakov et al, 2006, Ramnarine et al 2012):

1. Autotrophic soil respiration – associated with plant roots and their symbiotic microorganisms (e.g. mycorrhizal fungi).

2. Heterotrophic soil respiration – related to the process in which soil microorganisms decompose organic matter, releasing carbon dioxide (CO_2) into the atmosphere

Soils are large reservoirs of carbon, capable of exchange with the atmosphere (Lal, 2004). Carbon in soils can be divided into two main types: organic carbon and inorganic carbon (Gallagher and Breecker, 2020). Soil carbon in the form of carbonates may be an additional potential source of CO_2 emitted from soils to the atmosphere (Cardinael et al., 2020; Tamir et al. 2011).

The amount of $CO_{2(emi)}$ emitted into the atmosphere is the sum of carbon dioxide originating from the mineralization of organic compounds and from the dissolution of carbonates (Cardinael et al., 2020):

$$CO_{2(emi)} = SOC{-}CO_2 + SIC{-}CO_2, \qquad (15)$$

The mechanism of CO_2 reaction with soil water is presented in equation 1 in point 3.1.

There is likely a coupling mechanism between CO_2 released by microbial respiration and CO_2 derived from soil carbonate dissolution (Karberg et al. 2005). The increase in CO_2 concentration due to microbial respiration is considered to be the main factor responsible for carbonate dissolution (Kuzyakov et al. 2006; Rovira and Vallejo 2008). Carbonate decomposition occurs according to Equations 3–5 and may confound the soil respiration signal (Gallagher and Breecker, 2020).

Results from numerous studies indicate that liming can lead to an increase in soil respiration (Dong et. al. 2014, Borges et al. 2019, Fuentes et al., 2006; Bezdicek et al., 2003). In his study, Dong (2014) found that soil moisture and carbonate content had a significant effect on CO_2 emissions and this is related to soil microbial activity. The respiration effect in closed containers is influenced by both physical processes such as soil moisture (Dong et al., 2014), chemical processes (Borges et al., 2019) and an increase in soil microbial activity (Fuentes et al., 2006; Bezdicek et al., 2003). Soils of arid and semi-arid regions with pH > 8.5 and high calcium and/or magnesium abundance may increase SIC content after organic fertilisation and thus increase the amount of CO_2 emitted from soil respiration processes (Wang et al. 2015, Zamanian et al. 2016). Research by Gallagher and Breecker (2020) suggests that both dissolution and formation of calcium carbonate can reduce or overestimate soil CO_2 during and after increased microbial activity, respectively. Dissolution of calcium carbonate was observed in the first 30 hours after moistening the soil containing the calcium carbonate additive. The CO_2 concentration was up to 72% lower than that of a control soil sample containing no $CaCO_3$ The experiment was conducted in the laboratory under controlled environmental conditions.

7. SUMMARY AND CONCLUSIONS OF THE REVIEW

The important role of calcium carbonate, such as regulating soil pH, the C-cycle, providing Ca^{2+}, influencing soil fertility and increasing SOC stability through Ca^{2+} bridges, deserves increasing attention (Zamanian et al., 2021).

- the effect of $CaCO_3$ on CO_2 is strongly dependent on pH, humidity, temperature and biological activity.
- decomposition of $CaCO_3$ occurs mainly under acidic conditions and after the application of nitrogen fertilisers.
- stabilisation of organic matter by Ca^{2+} can reduce long-term CO_2 emissions.

In a meta-analysis, Wang (2021) analysed 1570 observations reported in 121 field studies worldwide to assess the effects of liming on soil greenhouse gas fluxes and plant productivity. He found that liming significantly increased crop yields and increased soil organic carbon (SOC) stores by 4,51% per year, although soil respiration was also stimulated (7,57%).

One of the key problems is the lack of clear separation between CO_2 emissions from biological processes (respiration of microorganisms and plants) and chemical emissions resulting from the reaction of $CaCO_3$ with organic or inorganic acids. Under natural conditions, these two sources often overlap, leading to an underestimation of CO_2 emissions from soils.

Further research into the differential role of inorganic carbon in soil CO_2 balance will provide valuable information to enable informed decisions regarding the carbon status of different soil types, facilitating the implementation of practices aimed at improving carbon sequestration and contributing to sustainable agronomic practices.

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