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CO_2 emission affected by moisture content and aggregate sizes in a calcareous soil of Comarca Lagunera, Mexico

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ABSTRACT: Soil CO_2 emissions are formed from biotic and abiotic processes related to organic carbon (SOC) and inorganic carbon (SIC), respectively. Calcareous soil has a high amount of SIC and occurs mainly in arid areas, and little is known about CO_2 emissions from aggregates of this soil. This study aims to evaluate the emission of CO_2 of aggregates from calcareous soil in the Comarca Lagunera, Mexico. Soil samples were taken from the layers of 0.00-0.15 and 0.15-0.30 m, and soil physical and chemical properties were determined. Aggregates distribution was obtained using the dry-sieving method. Macro (0.25–0.149 mm), meso (0.149–0.074 mm) and microaggregates (<0.074 mm) were selected for incubation in a dynamic closed system for 30 days under two moisture contents (15 and 30 %, dry weight basis). The CO_2 emissions were quantified using a non-dispersive infrared gas analyzer (IRGA). From total carbon measured, 97 % were found to be SIC. Soil texture is a sandy clay loam with a field capacity and a permanent wilting point of 27 and 17 %, respectively. From whole soil aggregates, 60 % were distributed in fractions lower than 0.25 mm diameter, which are highly erodible by the wind. Soil moisture content had a significant effect on the emission of CO_2. The highest accumulated CO_2 emission was registered in the superficial layer (0.00-0.15 m) within 0.25 mm aggregates (29.4 g m^{-2} h^{-1}), which turned out higher than reported for similar areas. The CO_2 emissions were attributed to the dissolution - reprecipitation process of high concentrations of SIC present in soil, involving a considerable contribution of CO_2 to the atmosphere.

Keywords: soil respiration, soil incubation, soil carbonates, soil moisture.

INTRODUCTION

Soil contains two forms of carbon: SOC (soil organic carbon) and SIC (soil inorganic carbon) (Mikhailova et al., 2019), and it is considered the third-largest carbon deposit on the planet; therefore it has a key role in this element's cycle (Wang et al., 2012). The amount of carbon stored is estimated to be 1220–1576 Pg for SOC and 700–1700 Pg for SIC in the first 1.00 m of soil (Guo et al., 2016). The largest amount of carbon in soil is stored organically, but in arid and semiarid areas, inorganic forms are more abundant, mainly in carbonates (Wang et al., 2012).

Soil CO_2 emissions comprise both biotic respiration related to SOC, and abiotic geochemical CO_2 exchange related to SIC (Wang et al., 2020). Incubation in a closed system is a common technique to measure CO_2 emission from soil (Pumpanen et al., 2000). As a main component of SOC, organic residues are used by the soil biotic component for its maintenance, a process known as mineralization in which CO_2 emissions are generated into the atmosphere (Kuzyakov, 2006). Environmental factors such as soil moisture regulate the mineralization of soil organic matter (SOM) since moisture deficiencies can suppress the activity of the microorganisms (Luo and Zhou, 2006).

Soil CO_2 emissions are commonly assumed in terms of SOC (Hannam et al., 2019), and SIC has been less studied, but it has currently taken relevance as it is identified as a clear contributor to CO_2 emissions, mainly in calcareous soils (Kuzyakov et al., 2018). Calcareous soils cover up to 30 % of earth's surface and are characterized for having a higher amount of SIC than SOC (Dong et al., 2014). In Mexico, these soils are found predominantly in arid areas of the north (Krasilnikov et al., 2013).

Soil carbonates can naturally dissolve and release CO_2 into the atmosphere (Ramnarine et al., 2012), which has implications for the exacerbations of climate change (Raich and Tufekciogul, 2000). Luo and Zhou (2006) mention factors affecting soil CO_2 emissions, such as soil moisture, temperature, oxygen, nitrogen, texture, and pH. Monger et al. (2015) and Sanderman (2012) explained CO_2 emissions from calcareous soils by process of dissolution – reprecipitation of calcium carbonates, as shown in equation 1.

Respiration   Rain or irrigation

$$CO_2 + H_2O$$
$$\Updownarrow \qquad \text{Eq. 1}$$
$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

Carbonates are dissolved in carbonic acid to produce Ca^{2+} and $2HCO_3^-$. Reprecipitation implies the use of $2HCO_3^-$ to form $CaCO_3$ again. However, reprecipitated carbonate does not capture atmospheric carbon because the source of calcium is the preexisting $CaCO_3$ and the CO_2 consumed in the reaction to form carbonic acid is released after reprecipitation of $CaCO_3$ (Drees et al., 2001).

Equation 1 shows the dissolution process – reprecipitation of carbonates, moisture content, whether by rain or irrigation, plays an important role. Several reports showed increases in CO_2 emissions in calcareous soils as soil moisture increases (Dong et al., 2014). Vargas et al. (2012) found high CO_2 emissions from soils in arid grasslands as a response to frequency and amount of rainfall as a source of moisture.

The arid areas of northern Mexico have been documented as fragile ecosystems, in which soil degradation due to changes in the ground cover makes them susceptible to wind erosion (López-Santos and Martínez-Santiago, 2015; Galloza et al., 2017). These soils are composed of aggregates with diameters less than 0.25 mm, considered a highly wind-erodible fraction (Shao, 2008; Zobeck and Van Pelt, 2014).

Comarca Lagunera is a region located in northern Mexico composed of five municipal areas of the state of Coahuila and ten municipal areas of the state of Durango (Guzmán-Soria et al., 2006), and cover a surface of 42,328.48 km^2, in which calcareous soils account for 32 %. This study aimed to evaluate the emission of CO_2 from aggregates of calcareous soil in the Comarca Lagunera, Mexico, under two moisture contents.

MATERIALS AND METHODS

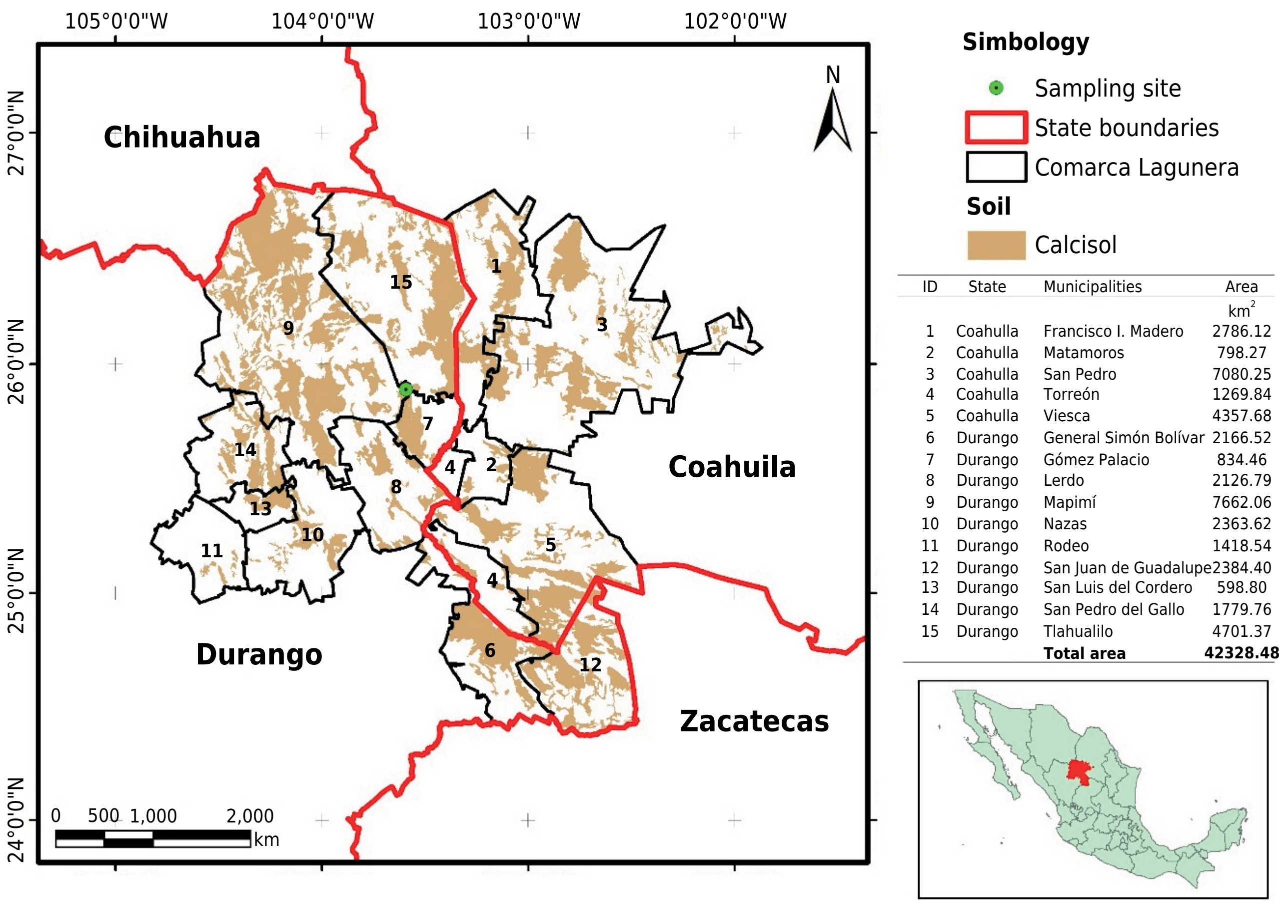
Sampling

Following the NOM-021-RECNAT-2000 (DOF, 2002), composite samples were taken from a calcareous soil in northern Mexico, at layers of 0.00-0.15 and 0.15-0.30 m, in the arid region known as Comarca Lagunera (Figure 1). Soil samples were taken in a zigzag pattern along an agricultural area of 80 hectares, 25° 53' 51" N and 103° 35' 37" W, where corn (*Zea mays*) was growing.

Determination of chemical and physical properties

The following physico-chemical and chemical properties were determined: pH and electric conductivity (EC) in a soil extract saturated with water, at a ratio of 1:2 (Alexakis et al., 2015); SOC determined by wet oxidation method (Walkley and Black, 1934); SIC determined by water displacement method (Horton and Newsom, 1953); soil total nitrogen (STN) by Kjeldahl method (Bremner, 1996) and carbon/nitrogen ratio (C/N).

The following physical properties were determined: bulk density (BD), using the clod method (Al-Shammary et al., 2018); particle density (PD), by pycnometer method (Flint and Flint, 2002); field capacity (FC) and permanent wilting point (PWP), by pressure plate



ID	State	Municipalities	Area km^2
1	Coahulla	Francisco I. Madero	2786.12
2	Coahulla	Matamoros	798.27
3	Coahulla	San Pedro	7080.25
4	Coahulla	Torreón	1269.84
5	Coahulla	Viesca	4357.68
6	Durango	General Simón Bolívar	2166.52
7	Durango	Gómez Palacio	834.46
8	Durango	Lerdo	2126.79
9	Durango	Mapimí	7662.06
10	Durango	Nazas	2363.62
11	Durango	Rodeo	1418.54
12	Durango	San Juan de Guadalupe	2384.40
13	Durango	San Luis del Cordero	598.80
14	Durango	San Pedro del Gallo	1779.76
15	Durango	Tlahualilo	4701.37
		Total area	**42328.48**

Figure 1. Calcareous soil sampling site in the Comarca Lagunera, Mexico.

and membrane method (Klute, 1986); texture, by the Bouyoucos method (Bouyoucos, 1951); distribution of net soil aggregates, using dry-sieving method (Díaz-Zorita et al., 2002) and mean weight diameter (MWD) (Kemper and Rosenau, 1986) using equation 2:

$$MWD = \sum_{i=1}^{n} \bar{x}_i w_i \qquad \text{Eq. 2}$$

in which MWD is the sum of products of the mean diameter ($\bar{x}_i$) from each size intervals and corresponding intervals (w_i) (van Bavel, 1950).

Soil incubation and quantification of CO_2 emission

Based on a generalized random block experimental design (Addelman, 1969), 100 g of soil were incubated in 500 mL closed glass jars for 30 days. Layers of sampling (0.00-0.15 and 0.15-0.30 m) and macro (0.25–0.149 mm), meso (0.149–0.074 mm) and microaggregates (<0.074 mm) were considered. Two gravimetric moisture contents, 15 and 30 %, with three replicates, which represented the permanent wilting point (1500 kPa) and field capacity (33 kPa) were applied (Figure 2). Moisture levels were kept constant by weighing the glass jars every two days and adding distilled water to replace the losses due to evaporation. Potential CO_2 emission was quantified every two days using a PP Systems infrared gas analysis (IRGA) equipment (Hitchin, Herts, UK).

Statistical analysis

Cumulative CO_2 emission data were subjected to an analysis of variance (ANOVA) and the average values were compared using a Tukey test ($\alpha = 0.05$) with statistical software R (Version 3.6.1; Vienna, Austria).

RESULTS

Physical, physico-chemical and chemical properties

Average values for pH(H_2O) (8.1 ± 0.1) and EC (6.4 ± 1.6 dS m^{-1}) indicated moderate alkalinity and slight salinity (Smith and Doran, 1996; Chesworth, 2008). Average SIC accounted for 97.7 % of total average carbon with 166.8 ± 37.5 Mg ha^{-1}, whereas average SOC content accounted for only 2.3 % with 3.9 ± 0.7 Mg ha^{-1}. Total soil nitrogen (TSN) had an average concentration of 0.12 ± 0.01 % (1.2 ± 0.1 mg g^{-1}) that represents 2.4 ± 0.1 Mg ha^{-1}. The carbon/nitrogen ratio had an average value of 1.6 ± 0.2 (Table 1).

Average values of 1.4 ± 0.6 Mg m^{-3} were for bulk density and 2.4 ± 0.1 Mg m^{-3} for particle density; 27.5 ± 0.4 and 14.4 ± 0.4 % to field capacity and permanent wilting point, respectively (Table 2), which are according to sandy clay loam texture (Saxton and Rawls, 2006). For the Comarca Lagunera, Inzunza-Ibarra et al. (2018) reported similar values.

In both depths, 39.6 % of soil aggregates was distributed within a range of 6.36 to 0.25 mm, while the remaining 60.4 % was made up of aggregates with diameters below 0.25 mm (Table 3). The mean weight diameter (MWD) was 1.20 ± 0.3 units, and, according to Le Bissonnais (2016), shows a low condition of stability and moderate crusting.

Soil aggregates ≤0.25 mm, at both depths, 23.5 % were distributed in size intervals 0.25-0.149 mm, 48.5 % between 0.149-0.074 mm, 27.4 % in fractions between 0.074-0.043 mm and 0.6 % in fractions below <0.043 mm (Table 4).

CO_2 emission rate

General average emission of CO_2 for every two days under both moisture contents was 1.7 ± 0.2 g m^{-2} h^{-1}, or using conversion units proposed by Lamptey et al. (2017), 10.7 ± 0.2 μmol m^{-2} s^{-1}. Highest emission value was reached with 30 % of moisture content after 8 days of incubation (Figure 3b), with 2.1 ± 0.1 g m^{-2} h^{-1} (13.3 ± 0.3 μmol m^{-2} s^{-1}), and

Figure 2. Generalized random block experimental design for soil incubation with two gravimetric moisture levels.

Table 1. Physico-chemical and chemical properties of soil samples from La Comarca Lagunera, Mexico

Layer	pH	EC	SOC	SIC	STC	STN	SOC	SIC	STC	N	C/N
m		*dS m*$^{-1}$	%				*Mg ha*$^{-1}$				
0.00-0.15	8.1	7.7	0.23	7.3	7.5	0.13	4.4	140.4	144.8	2.5	1.8
0.15-0.30	8.0	5	0.16	9.1	9.3	0.11	3.4	193.3	196.7	2.3	1.5
Avg	8.1	6.4	0.20	8.2	8.4	0.12	3.9	166.8	170.7	2.4	1.6
	±	±	±	±	±	±	±	±	±	±	±
SD	0.1	1.6	0.05	1.1	1.2	0.01	0.7	37.5	36.7	0.1	0.2

EC: electric conductivity; SOC: soil organic carbon; SIC: soil inorganic carbon; soil total carbon (STC) = SOC + SIC; STN: soil total nitrogen; C/N: carbon/nitrogen ratio; Avg: average; SD: standard deviation.

Table 2. Physical properties of soil samples from the Comarca Lagunera, Mexico

Layer	BD	PD	FC	PWP	Texture
m	Mg m^{-3}		%		
0.00-0.15	1.3	2.5	27.2	14.6	Sandy clay loam
0.15-0.30	1.4	2.4	27.7	14.1	Sandy clay loam
Avg	1.4	2.4	27.5	14.4	
	±	±	±	±	
SD	0.6	0.1	0.4	0.4	

BD: bulk density; PD: particle density; FC: field capacity; PWP: permanent wilting point; Avg: average; SD: standard deviation.

Table 3. Distribution of aggregates and mean weight diameter of soil samples from La Comarca Lagunera, Mexico

Layer	Sieve (mm)								MWD
	> 6.36	6.36-4.76	4.76-3.36	3.36-2	2-1	1-0.5	0.5-0.25	< 0.25	
m	%								
0.00-0.15	7	0.1	1.7	2.8	5.8	9.6	6.9	66.0	0.9
0.15-0.30	11	0.9	4.7	5.1	7.3	10.4	5.9	54.8	1.5
Avg	9	0.5	3.2	3.9	6.6	10.0	6.4	60.4	1.2
	±	±	±	±	±	±	±	±	±
SD	2.8	0.5	1.7	1.3	0.9	0.5	0.6	6.6	0.3

MWD: mean weight diameter; Avg: average; SD: standard deviation.

Table 4. Distribution of aggregates ≤0.25 mm of soil samples from the Comarca Lagunera, Mexico

Layer	Sieve				
	0.25-0.149 mm	0.149-0.105 mm	0.105-0.074 mm	0.074-0.043 mm	<0.043 mm
m	%				
0.00-0.15	23.7	14.3	40.9	20.9	0.2
0.15-0.30	23.4	13.1	28.7	33.9	0.9
Avg	23.5	13.7	34.8	27.4	0.6
	±	±	±	±	±
SD	0.2	0.8	8.6	9.2	0.5

Avg: average; StD: standard deviation.

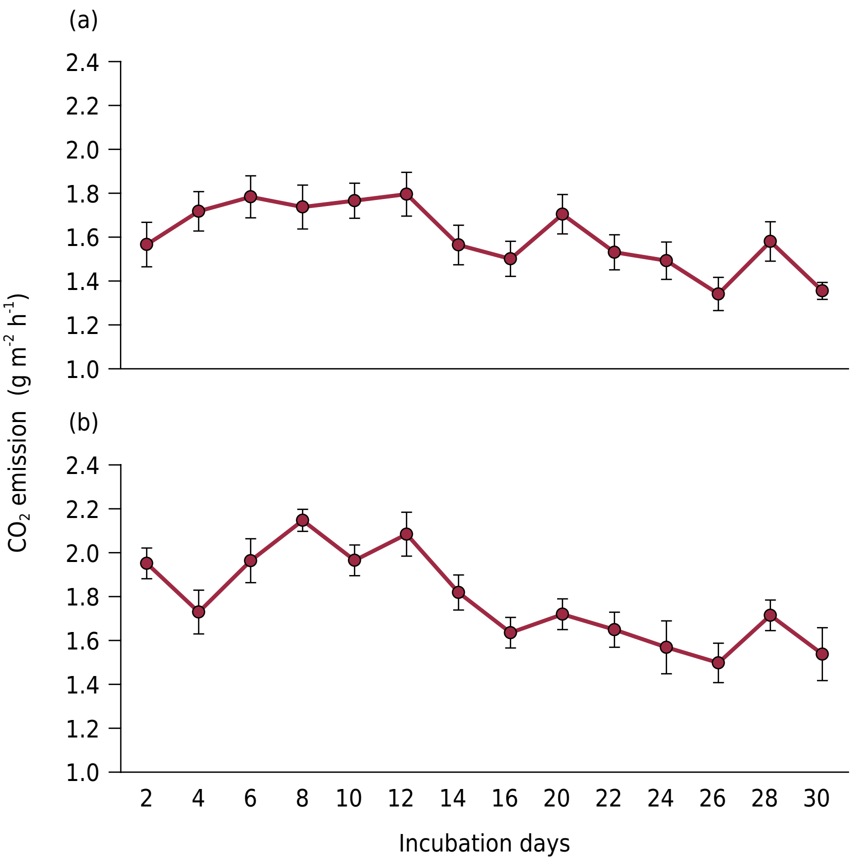


Figure 3. Average CO_2 emission rate under 15 % (a) and 30 % (b) moisture treatments for a calcareous soil in the Comarca Lagunera, Mexico.

the lowest, with 15 % of moisture content, after 26 days (Figure 3a), with 1.3 ± 0.1 g m^{-2} h^{-1} (8.2 ± 0.6 μmol m^{-2} s^{-1}).

Accumulated rate of CO_2 emission

The average accumulated emission of CO_2 of soil aggregates increased significantly by 2.5 g m^{-2} h^{-1} equivalent to 11 %, from 22.5 ± 0.9 to 25 ± 1.1 g m^{-2} h^{-1}, as soil moisture increased (Figure 4).

Accumulated emission of CO_2 by depth and aggregates size

Accumulated emission at a layer of 00.00-0.15 m was significantly higher in macroaggregates (0.250-0.149 mm), with a value of 26.4 ± 2 g m^{-2} h^{-1}. Mesoaggregates (0.149-0.074 mm) had an emission of 24.4 ± 1.7 g m^{-2} h^{-1}, and the microaggregates (<0.074 mm) had the lowest, with 22.7 ± 0.8 g m^{-2} h^{-1} (Figure 5). Accumulated CO_2 emission of soil macro, meso and microaggregates of the layer of 0.15-0.30 m were statistically similar to emissions from microaggregate at the layer of 0.00-0.15 (Figure 5).

Accumulated emission of CO_2 by aggregate size, layer and moisture content

Macroaggregates (0.25-0.149 mm) at 0.00-0.15 m layer with 30 % moisture showed the highest accumulated emission with 29.4 ± 1.5 g m^{-2} h^{-1}. The lowest emission was

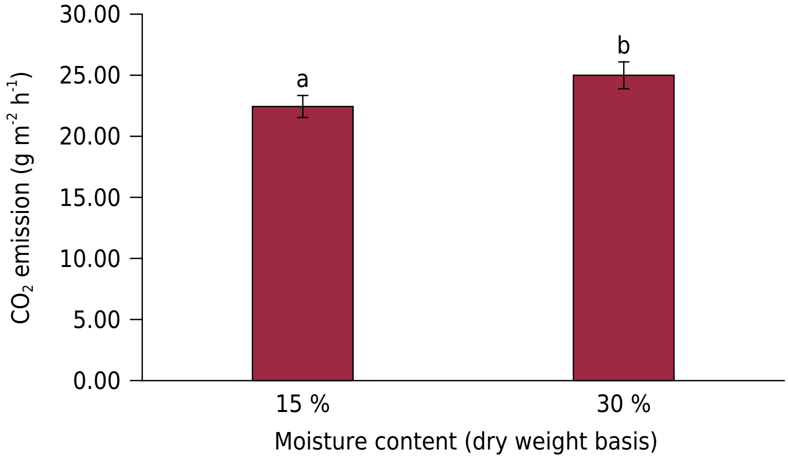


Figure 4. Accumulated emission of CO_2 of a calcareous soil with two moisture contents in the Comarca Lagunera, Mexico.

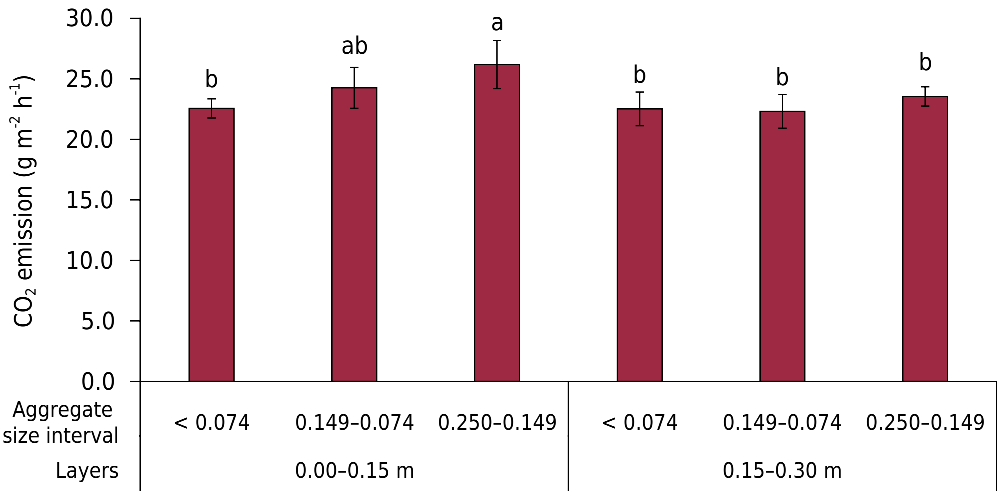


Figure 5. Accumulated emission of CO_2 by layer and aggregates size of a calcareous soil in the Comarca Lagunera, Mexico.

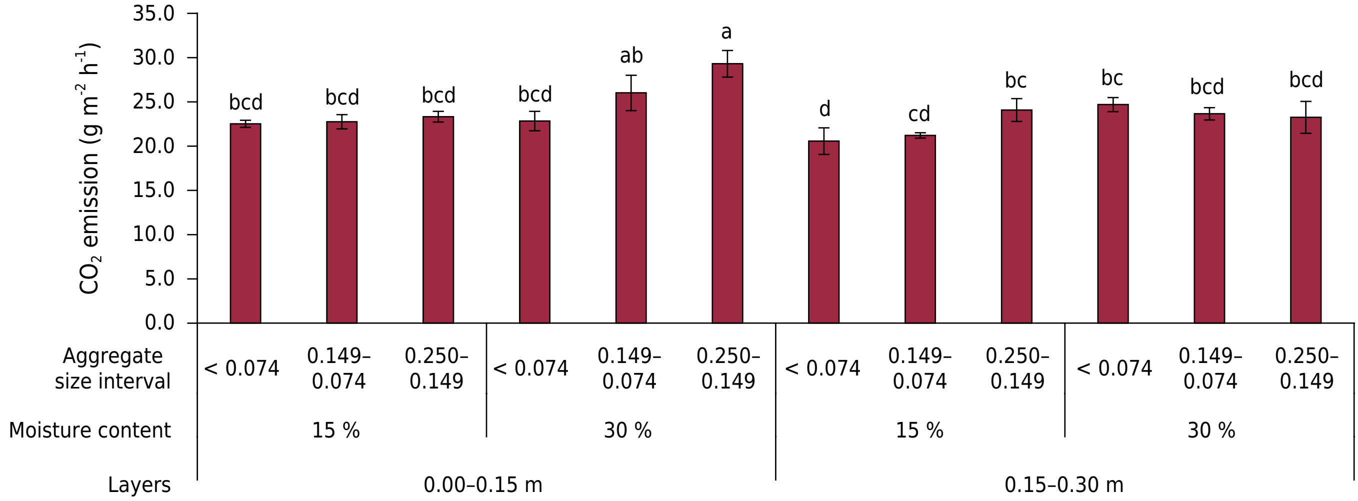


Figure 6. Accumulated emission of CO_2 by aggregate size, level of moisture and depth in a calcareous soil of the Comarca Lagunera, Mexico.

with microaggregates (<0.074 mm) and 15 % of moisture, and for 0.15-0.30 m layer, had value of 20.6 ± 1.5 g m^{-2} h^{-1} (Figure 6). As soil depth increases and moisture level decreases, less CO_2 is emitted, which is clear in aggregates of smaller diameters

DISCUSSION

Soil properties of calcareous soils from the Comarca Lagunera

Calcareous soils of arid areas have alkalinity and salinity conditions (Zhao et al., 2016), as well as the presence of large amounts of SIC (Mikhailova et al., 2019) and low levels of SOC and STN (Aboukila et al., 2018), as detected in the present study (Table 1).

Values obtained for BD, FC and PWP of the calcareous soils of the Comarca Lagunera (Table 2) are similar to those previously reported by Inzunza-Ibarra et al. (2018). Distribution of soil aggregates shows that 60.4 % of total soil aggregates ≤0.25 mm (Table 3), which is associated with the low content of SOC that prevents the existence of organic binding agents (Qiu et al., 2015; Jia et al., 2019). This aggregates size (≤0.25 mm) is considered by Chepil (1953) as a highly wind-erodible fraction.

Emissions of CO_2 of calcareous soils from the Comarca Lagunera

Average CO_2 emission showed increases after the maximum emission, on day 20 (Figure 3), due to keeping the initial level of the moisture content, which has been documented as Birch effect (1958) and implies pulses in soil respiration rate when it is rehydrated. The Birch effect has been reported, both in controlled incubation (Göransson et al., 2013) and in the field (Yan et al., 2014).

In calcareous soils of the Comarca Lagunera, average CO_2 emissions were 10.70 µmol m^{-2} s^{-1}, contrasting with studies reported for the Chihuahuan desert in the Big Bend National Park, where a CO_2 emission of 1.46 µmol m^{-2} s^{-1} was reported, despite soil contains 3.7 % (37 mg g^{-1} of C) of SOC (Cable et al., 2011). Quantification of CO_2 emissions from soils considers primarily the degradation of SOC reserves (Kuzyakov, 2006), which integrates organic residues and soil microorganisms, as they are related to anthropogenic activities, but for arid zones, it must add the contribution of the SIC to CO_2 emissions (Zamanian et al., 2021), because the amounts of stored SIC exceed those of SOC by several times (Ferdush and Paul, 2021).

On average, SOC content was 0.20 % (2 mg g^{-1}), and most of the CO_2 emissions could be attributed to the dissolution of SIC, which was 8.2 % (82 mg g^{-1}). This situation has been documented by Aryal et al. (2017) for calcareous soils of Mexican tropics, where the dissolution of carbonates is the main source of variation in CO_2 emission. Incubations of calcareous soil performed by Dong et al. (2013) found that CO_2 emissions are related to amounts of carbonates.

Soil moisture influences CO_2 emissions, involving biological activity on the decomposition of organic matter (Lellei-Kovács et al., 2011), and contributes to the process of dissolution – reprecipitation of carbonates (Equation 1) belonging to SIC (Monger et al., 2015). The CO_2 emitted by the degradation of SOC also can form carbonic acid, which intervenes in the dissolution of SIC (Cardinael et al., 2020).

In this study, soil moisture near field capacity (30 %) in macroaggregates of topsoil layer produced 29.4 g m^{-2} h^{-1} (185.3 μmol m^{-2} s^{-1}), the highest accumulated emission of CO_2 (Figure 6), which represents a loss of 1.9 Mg ha^{-1} of carbon in the soil, equal to 1.33 % of total carbon in the layer between 0.00-0.15 m. Considering calcareous soils under agricultural use in the Comarca Lagunera with an extension of 182,002.75 ha, soil carbon loss is around 349,445.3 Mg (349.45 Gg).

The CO_2 emissions from the topsoil layer (0.00-0.15 m) and macroaggregates are produced due to content of SOC and STN (Yu et al., 2014; Gomiero, 2016; Welemariam et al., 2018), which implies certain amount of labile organic carbon that microorganisms can mineralize (An et al., 2010). However, it is important to consider the CO_2 emissions resulting from the dissolution of SIC reserves (Zamanian et al., 2016). Besides, in calcareous soils, 60 to 80 % of the total CO_2 emissions are produced by the dissolution of the SIC (Ramnarine et al., 2012).

On the other hand, the acidification of agricultural soils due to ammonium fertilization leads to a CO_2 release by dissolving soil carbonates (Wu et al., 2009; Jin et al., 2018; Zamanian et al., 2018). In the Comarca Lagunera, agricultural management of fodder crops implies the use of higher rates (>300 kg ha^{-1}) of ammonia fertilizers than those required (González-Torres et al., 2016).

Sources of SOC and SIC play a crucial role in the aggregation and stability of the soil (Bronick and Lal, 2005; Su et al., 2010), and their loss could contribute to soil degradation (Ćirić et al., 2012). For soils of the Comarca Lagunera, given a scarce SOC most common aggregates have diameters less than 0.25 mm, and according to Chepil (1953) they are within the highly erodible fraction.

Actions to mitigate the increase in atmospheric CO_2 concentration related to carbon capture through SOC should be reviewed (Raza et al., 2021), mainly in calcareous soils, since the emission of CO_2 generated because of dissolution of the SIC reserve are considerable and influences the carbon cycle and global warming (Zamanian et al., 2018). To increase knowledge on calcareous soils in Mexico is needed, including additional studies about structural characteristics and chemical composition, with particular emphasis on SOC and SIC relationship.

CONCLUSIONS

Main soil aggregate size was ≤0.25 mm, which are characterized by being highly wind-erodible and typical of arid and semi-arid areas. Macroaggregates by retaining more moisture allowed the higher release of CO_2 in the surface layer. This study shows predominance of SIC over SOC and implies an increase in the proportion of CO_2 emissions into the atmosphere. The increase in CO_2 emissions was associated with the moisture content between permanent wilting point and field capacity. The results suggest SIC content in arid and semiarid areas could depend on the moisture content for the dissolution and reprecipitation process as a cause of CO_2 emissions.

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