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Research article

Dynamics of soil organic and inorganic carbon in southern Tunisia

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Abstract
SOC (Soil Organic Carbon) and SIC (Soil Inorganic Carbon) are important carbon stocks in arid and semi-arid regions. However, previous studies have mainly focused on the SOC, while limited information has been provided about the rate of carbon sequestration as secondary carbonates (SC). The aim of the study is to understand the vertical distribution of SIC and assess its role in carbon sequestration in the cropland of the South Tunisia. Eighty soil samples were collected from 16 profiles, from two oases: Guettaya continental oasis and Cheneni coastal oasis. The study was based on the measurements of SOC, SIC, soluble Ca^{2+} and Mg^{2+} contents. Our results showed that the mean SOC content averaged over 80 soil samples decreased from 10.25 $g.kg^{-1}$ near the surface to 5.63 $g.kg^{-1}$ in 80-100 cm whereas the mean SIC content is 15.13 $g.kg^{-1}$ in 0-20 cm, then it showed little vertical increase from 12.22 to 14.33 $g.kg^{-1}$ in the subsoil. There was a significantly positive correlation between SOC and SIC in the two oases Cheneni and Guettaya ($r = 0.89$ and $r = 0.77$, $p < 0.01$ respectively). Our results suggests that increasing SOC might lead to an increase in SIC stocks in the Tunisian oases.

Key words: Soil organic carbon, soil inorganic carbon, stock, oases, Tunisia.

1. Introduction

The stabilization of an increasing CO_2 concentration in the atmosphere is currently the world's major ecological concern (Brahim and Ibrahim 2018; Mishra et al. 2010). Carbon stock in soil is the transfer of atmospheric CO_2 in the soil pools, comprising the soil organic carbon (SOC) and soil inorganic carbon (SIC) components (Banger et al. 2009; Dong et al. 2017; Schmidt et al. 2011). Just like the SOC content, its evolution requires the study of the organic matter's dynamics in the long, medium and short terms (Ibrahim et al. 2016; Pansu et al. 2018). However, to study the inorganic carbon, it is important to monitor the carbonate dynamics. The global inorganic carbon pool represents roughly 35% of the total terrestrial carbon (organic and inorganic) pool. The global SOC pool is estimated at 2000-2500 Gt (27-36% in dryland areas), while SIC is 940 Gt as well as 97% in dryland areas (Table 1) (Bernoux and Chevalier 2004).

Table 1: SIC pool to 1-m depth in major soil orders and land types (Eswaran et al. 2000 Modified)

Order	Area (Mha)	SIC pool (Gt)
Alfisols	1262.0	43
Andisols	91.2	0
Aridisols	1569.9	456
Entisols	2113.7	263
Gelisols	1126.0	7
Histosols	152.6	0
Inceptisols	1286.3	34
Mollisols	900.5	116
Oxisols	981.0	0
Spodosols	335.3	0
Ultisols	1105.2	0

Vertisols	316.0	21
Shiftingsand	532.2	5
Rocky land	1307.6	0
Total	13079.5	**940**

Soil carbon is not always associated with organic matter; there is also an inorganic carbon component in soils. Taking the latter into consideration is very important for arid areas because calcification and secondary carbonates (SC) formation is an important environmental phenomenon (Batjes and Sombroek 1997). In closed zones, the sequestration of inorganic carbon occurs by the movement of HCO_3. On the other hand, the inorganic carbon in the soil is relatively stable; nevertheless, this inorganic form in contact with water (water erosion) releases atmospheric CO_2.

In recent research, several authors consider solid carbonate as a SIC sink (Lal and Kimble 2000a, 2000b), while others consider the dissolution of solid carbonate as sequestration of SIC due to the partially leached dissolved carbon, which becomes unavailable for a long time (Drees et al. 2001). It is well known that soil carbonate effects the soil properties (pH, water retention capacity, soil fertility, etc.). The pH of carbonate soils is basic in arid areas, while Ca^{2+} ions act as a soil stabilizing factor. Similar to organic carbon, Inorganic carbon can be influenced by human activities (Wu et al. 2009; Lal et al. 2015). In 1999, Lal and Bruce studied an atmospheric CO_2 precipitation and the formation of pedogenic carbonates. They estimated that it occurs at a rate of 0.007-0.266 Gt of carbon/year in arid and semi-arid regions.

Studies have shown that relatively acidic natural precipitation increases the loss of CO_2 and reduces the carbonate content of the soil. Other results suggest that irrigation in semi-arid regions can lead to sequestration of inorganic carbon in the soil. However, some recent research has shown that in arid and semi-arid regions, both SOC and SIC stocks were greater in agricultural lands than in non-agricultural lands (Mikhailova and Post 2006; Su et al. 2010). Exchanges between different forms of carbon depend on several factors (climate, land use patterns, cultural variations, etc.). As a result, it is still very difficult to find a precise relationship between SIC and SOC. Not much effort has been done to estimate SIC stocks, despite the important role carbonates play in the dynamic changes of the environment, atmosphere, vegetation and soil. Previous work has shown a relationship between SIC and SOC. This correlation can be either positive or negative depending on soil properties and climatic conditions. The mechanisms of the variations in SOC and SIC under different types of vegetation (high fertility and low fertility) are still poorly understood and require further study.

The objectives of this study are to examine the vertical distributions of both SOC and SIC and to evaluate the potential factors determining SIC dynamics in oases land of Tunisia. In order to do so, we selected a typical arid region in southern Tunisia: the Cheneni coastal oasis in Gabes with multi-layer vegetation cover under the date palms (high fertility), and Guettaya continental oasis in Kebili where the palms grow on bare soil (low fertility).

The forms of carbonates in soil

In carbonate rocks and soil, inorganic carbon is mainly in the form of calcite ($CaCO_3$) or, to a lesser extent, associated with magnesium (dolomite, $CaMg(CO_3)_2$). More occasionally, it may be found in other forms, e.g. sodium carbonate (Na_2CO_3) or siderite carbonate ($FeCO_3$), and other even more marginal forms. As illustrated in figure 1, the materials may be primary-carbonates (PC), which are derived from the parent material (lithogenic carbonates) or SC which are formed through the reaction of atmospheric CO_2 with Ca^{+2} and Mg^{+2} (Lal and Kimble 2000) (pedogenic carbonates). Pedogenic carbonates may have very different forms (Ming, 2002). They are precipitated in soil pores, around roots, or in the form of nodules and crystalline minerals.

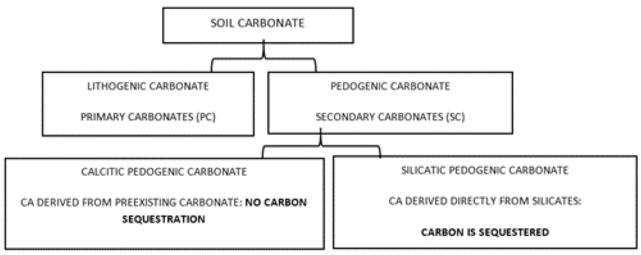

Figure 1. Classification of soil inorganic carbon

2. Materials and methods

2.1. Study sites and sampling

The study was conducted at the maritime Cheneni oasis which is located along the coast of the gulf of Gabes (33° 53' N, 10°12' E) in South-East Tunisia, and the continental oasis of Guettaya is located in the Kebili region in Southern Tunisia (33°40' N, 8°52' E). The oasis location is to the west and adjacent to Chott Djerid (a salt plain).

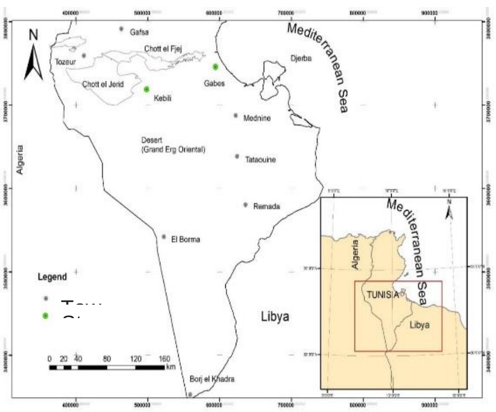

Figure 2. Localization of study areas (Gabes and Kebili) on Tunisia map

The soil sampling campaign in both oases was performed along a transect line at intervals of about 200 m starting at the oasis centre while moving outward till Gabes desert (in the case of the oasis of Cheneni) and the salt plain of Chott el Jerid (in the case Guettaya oasis of Kebili). Five samples were taken from 8 locations inside each oasis. The samples were dug at 5 different depths (0-20 cm, 20-40 cm, 40-60 cm, 60-80 cm and 80-100 cm). To minimize the effect of the sample locations, the soil was sampled from near trees, near trunks, under palm crowns, and between date palms. In total, 80 soil samples were collected from both oases.

2.2. Soil analyses

Soils were air-dried, well mixed and sieved to pass a 2-mm screen for the measurements of pH, electric conductivity (EC), soluble Ca^{2+} and Mg^{2+}. Soil pH and EC were measured using a soil:water (1:2.5) mixture. Soluble Ca^{2+} and Mg^{2+} were determined using a soil:water (1:5) mixture by an Atomic Absorption Spectrophotometer. Carbonate contents were determined by the method of calcimetry (Nelson and Sommers 1982). Carbonate contents were then converted into contents of inorganic carbon (IC). SOC was measured by the $K_2Cr_2O_7$-H_2SO_4 oxidation method of Walkey and Black (Nelson and Sommers 1982).

2.3. Statistical analysis

In the following, we present the objective measures we used to base our calculations and statistical analyses. For each soil site, SOC and SIC stocks (kg C m^{-2}) were calculated from carbon content (g C kg^{-1}), BD (Ei, g cm^{-3}) and thickness (Di, cm):

$$SOC = \sum_{i=1}^{n} SOC_i \times D_i \times {E_i}/_{100}$$

$$SIC = \sum_{i=1}^{n} SIC_i \times D_i \times {E_i}/_{100}$$

The standard deviation of the error was calculated for each parameter and at all depths. The relationships between the soil properties, SOC and SIC were assessed by means of Pearson's correlations ($p<0.01$) using SPSS statistics 20. Linear regression analyses were carried out to evaluate the relationships between SIC and other variables.

In order to evaluate the impacts of soil fertility on SIC stock, we examine the difference in vertical distribution of SIC between low and high fertility soils. According to Zhang et al. (2015), organic matter is often considered to be a key attribute of soil fertility. To that end, we separate the soil profiles into two groups: high fertility (Cheneni oases) and low fertility (Guettaya oases).

3. Results and discussion

3.1. Soil chemical properties

As shown in Table 2, soil pH in the study area ranged from 7.61 to 8.04. Soil electric conductivity was increased from 4.09 ms.cm^{-1} near the surface to 8.25 ms.cm^{-1} at a depth of 100 cm. Similarly, bulk density also showed an increasing trend with soil depth from 1.29 to 1.39. The mean of soluble Ca^{2+} and Mg^{2+} is 51.5 (0-20 cm) - 34.81 (80-100 cm) mg kg^{-1} and 22.56 (0-20 cm) - 23.25 (80-100 cm) mg kg^{-1}, respectively. We noticed a small variation in the means of these cations depending on the sample depth.

Table 2: Mean values (standard deviations) of soil pH, electric conductivity (EC), bulk density (BD), soluble Ca^{2+} and Mg^{2+}, soil organic carbon (SOC) and soil inorganic carbon (SIC) in different soil layers, averaged over 80 soil samples.

Soil depth cm	pH	EC mS.cm^{-1}	Ca^{2+} mg.kg^{-1}	Mg^{2+} mg.kg^{-1}	SOC g.kg^{-1}	SIC g.kg^{-1}
0-20	7.69 ± 0.1	4.09 ±0.72	51.5± 18.5	22.56 ± 9.17	10.25 ± 2.94	15.13 ± 2.77
20-40	7.61 ± 0.3	4.99 ±1.22	37.19 ± 19.84	22.46± 13.62	4.95 ± 1.8	12.22 ± 2.19
40-60	7.98 ± 0.2	5.7 ± 1.2	33.69 ± 17.5	21.13 ± 8.76	5.89 ± 1.85	13.4 ± 2.97
60-80	8.04 ± 0.2	7.58 ± 1.7	33.5 ± 15.27	19.13 ± 9.2	5.06 ± 1.93	12.34 ± 2.11
80-100	7.99 ± 0.3	8.25 ± 1.93	34.81 ± 19.45	23.25 ± 10.24	5.63 ± 1.87	14.33 ± 2.89

3.2. Vertical distributions of SOC and SIC

Figure 3 shows the vertical distribution of SOC and SIC in both oases. The figure 3 (a) and (c) demonstrates a wider range of SOC content around the surface (8.5 - 16.32 g.kg^{-1} for Cheneni oases and 6.46 - 11.93 for Guettaya oases) relative to the sub-soils (4.97 - 8.82 g.kg^{-1} and 2.9 - 7, respectively). It also illustrates a drastic decline in the SOC content at shallow depth (0 to 40 cm). The decline in the SOC content was not that significant in the sub-soils. The SOC variation with depth is also confirmed in Table 2 for both oases ($p< 0.01$).

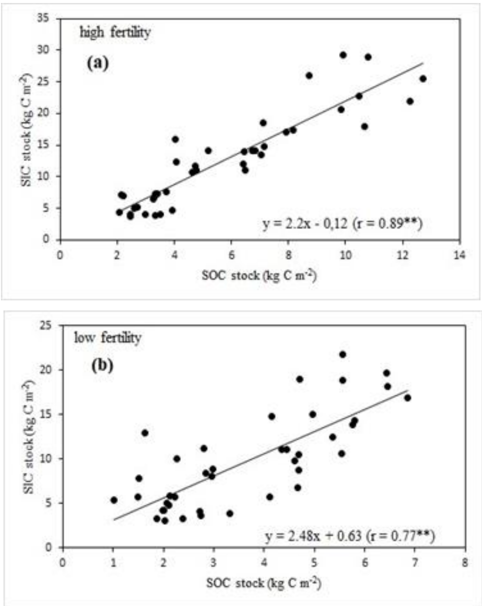

Figure 3: Vertical distributions of soil organic carbon (SOC) and soil inorganic carbon (SIC). (a), (b) : high fertility in Cheneni. (c), (d) : low fertility in Guettaya

As depicted in Figure 3 (b) and (d), the SIC content was generally higher than 15 g.kg^{-1} in Cheneni (high fertility) surface soil and higher than 12 g.kg^{-1} in Guettaya (low fertility). Unlike SOC, a slightly increasing trend of SIC content with depth was seen in the soil profiles. The range of SIC also increased from 13.64 to 15.83 g.kg^{-1} in subsoil (40-100 cm) of Cheneni and from 10.8 to 12.84 g.kg^{-1} in Guettaya oasis.

3.3. Relationship between SIC and SOC stocks

Both SOC and SIC have been reported to strongly interact with each other (Sahrawat 2003). Our analysis showed a positive correlation between SIC and SOC stocks over the 0-100 cm ($r = 0.89$, $p<0.01$ for Cheneni oasis and $r = 0.77$, $p<0.01$ for Guettaya oasis) in the soils of the two types of oases in Tunisia (figure 4 (a) and (b)). These results imply that the increase of SOC in an alkaline soil can lead to an increase of the SIC in the subsoil if there is no shortage of calcium (and magnesium).

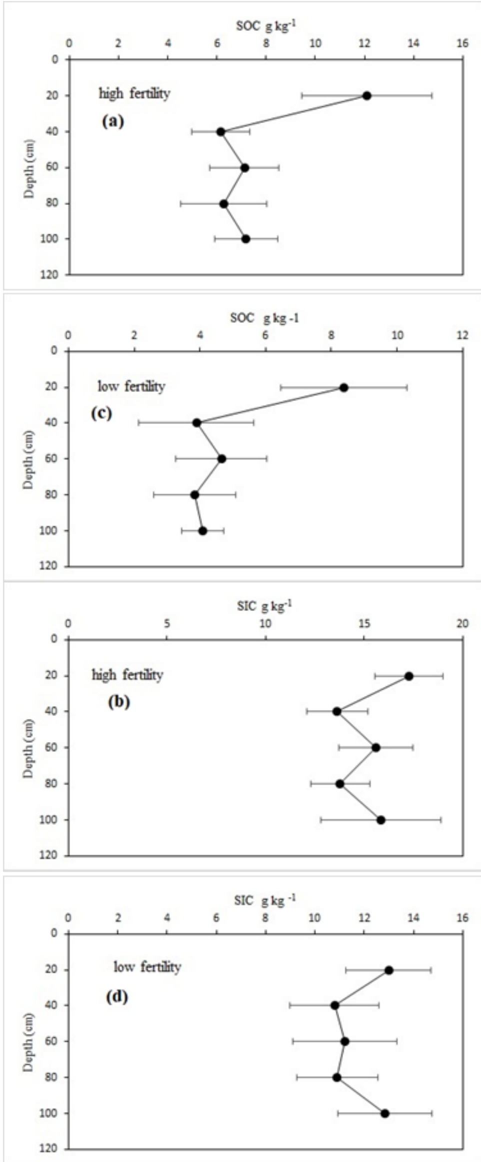

Figure 4: Relationship between soil organic carbon (SOC) and soil inorganic carbon (SIC). (a) : high fertility in Cheneni. (b): low fertility in Guettaya

Remarkably, Guo et al. (2016) reported a significantly positive relationship for both the topsoil and the 0-100 cm layer. However, some other studies showed that the relationship between SIC and SOC was negative in the surface soil of northern China (Li et al. 2010; Pan et al. 2000; Zhao et al.2016). It is clear that the relationship between SIC and SOC is complicated, which might reflect the decoupling of various processes related to the formation of carbonate over time and space (Zheng et al. 2011).

The dissolution and precipitation of carbonate involve two main reactions:

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

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

The biotic factor can influence $CaCO_3$ formation based on the soil CO_2 concentrations, pH, Ca^{2+} content and evapotranspiration. An increase in H^+ would provide acidic environments, which drives reaction (2) towards the left direction, which decreases the carbonate, leading to a negative relationship between SOC and SIC. On the other hand, a decrease in H^+ produces HCO_3^- which could drive reaction (2) to the right direction and produce SIC, resulting in a positive relationship between SOC and SIC (Wang et al. 2015).

The SIC pool, includes elemental carbon, PC and SC formed through the precipitation of newly induced carbonate material (Wu et al. 2009). As for the SC, it is categorised into two groups: calcitic secondary carbonates (CSC) and silicatic secondary carbonates (SSC), depending on the source of Ca^{2+} (Monger et al. 2015). CSC acquires Ca^{2+} from the dissolution of PC and the re-precipitation of dissolved ions. During the dissolution phase of PC, one mole of atmospheric CO_2 is consumed while one mole of CO_2 is re-emitted during the precipitation stage. In this process, carbon is not sequestered. On the other hand, the neoformation of SC occurs when two moles of CO_2 react with one mole of Ca^{2+} silicate. This can lead to the sequestration of atmospheric CO_2 in soils (Wu et al, 2009).

When soil pH >8, the soil condition is still alkaline, which would not let reaction (1) shift towards the left direction. As a result, HCO_3^- would remain in the soil profile. Because the majority of the soil in the arid and semi-arid regions has a pH > 8, a positive relationship would be more common (particularly over depths of 0-100 cm) in the oasis of southern Tunisia with no shortage of Ca^{2+} and/or Mg^{2+}, implying that an enhancement of SOC may lead to an increase in SIC. This hypothesis might be correlated to the difference in fertility and the vegetation cover of the two oases.

A previous study has proven that soil fertility (SOC) of semi-arid regions of China can significantly augment the carbonate accumulation (Jiang et al. 2006). Zhang et al. (2015) reported that SIC stock was modestly higher in high fertility soil than its low fertility counterpart. These findings suggest that increasing soil fertility may lead to enhanced carbonate accumulation in soil profile. To explore the impacts of soil fertility on SIC stock in the oases, we divided our data into two groups (low and high fertility profiles) using a criterion of 9.0 g kg^{-1} SOC within a depth of 0-20 cm, which was similar to that used in the Lanzhou area by Zhang et al. (2015) and Guo et al. (2016). These results were found to be in harmony with the studies presented in the current manuscript as we showed that the mean value of SIC content ranged from 13.64 g kg^{-1} to 17.27 g kg^{-1}in high fertility soils while it varied between 10.8 g kg^{-1} and 12.99 g kg^{-1} in low fertility soils. The value of SIC stock over 0-100 cm was significantly ($p< 0.01$) higher in the high fertility soils (22.54 kg C m^{-2}) than in the low fertility soils (17.85 kg C m^{-2}).

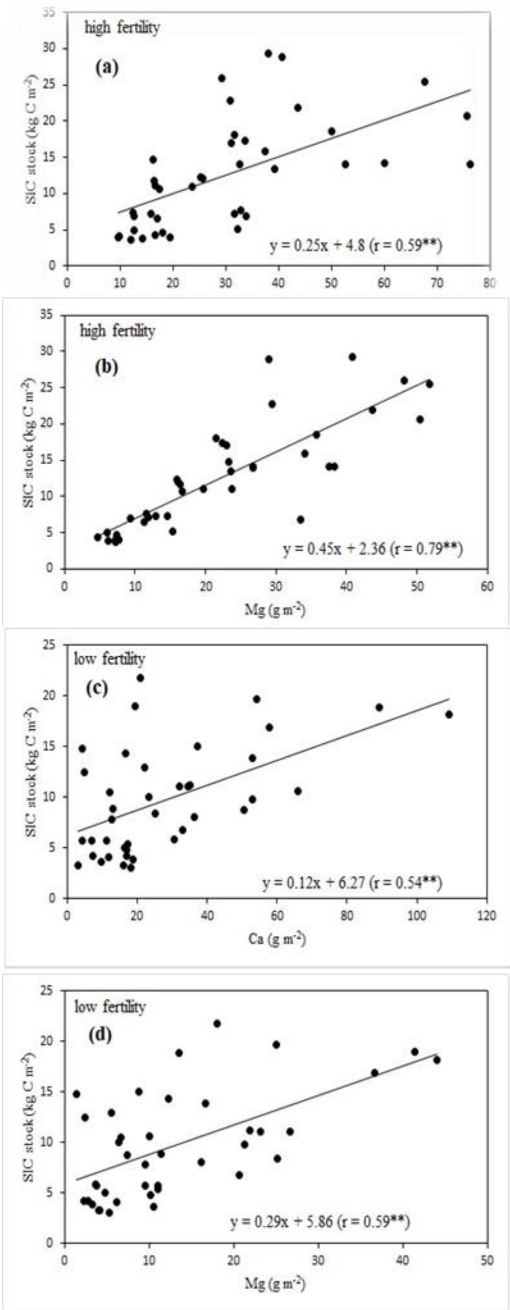

Figure 5: Relationship between soil inorganic carbon (SIC) and soluble ion (Ca^{2+} and Mg^{2+}) stocks. (a), (b) : high fertility in Cheneni. (c), (d) : low fertility in Guettaya

Our studies carried out in the South Tunisia provide new evidence that increasing soil fertility (particularly SOC) in the southern Tunisia's oases can lead to an augmentation in SIC formation particularly in the subsoil.

3.4. Relationship between SIC and Ca^{2+}or Mg^{2+}

Statistical analyses indicated that SIC stock had a significantly positive relationship with soluble Mg^{2+} and Ca^{2+} (figure 5). An increase in the two elements would drive reaction (2) to the right, leading to the precipitation of carbonate. Different studies showed that SIC was positively correlated with water soluble Ca^{2+} and Mg^{2+} (Guo et al. 2016; Shi et al. 2017). Our Data showed a strong relationship between SIC and cations (Ca^{2+} (r=0.59, p<0.01) / Mg^{2+} (r=0.79, p<0.01)) in Cheneni site (figure 5 (a), (b)), also a positive correlation in the Guettaya site (Ca^{2+} (r=0.54, p<0.01) / Mg^{2+} (r=0.59, p<0.01)) (figure 5 (c), (d)). It has been reported in the literature (Mlih et al. 2019) that the oases of Cheneni and Guettaya are comparable in many aspects, except in the fertility and the vegetation cover. We suspect that this might be behind the discrepancy in the SIC-cations relationship between the two oases (figure 5).

Further studies are needed to determine the various sources of Ca^{2+} and Mg^{2+}, and to quantify stocks and fluxes of various carbon forms in the arid and semi-arid regions, which aim to improve our understanding of the carbon cycle in the terrestrial ecosystems. However, research using 13C isotope technique and microscopy observation are required to further explain these mechanisms (Dong et al. 2017).

4. Conclusions

To the best of the authors' knowledge, this research is the first investigation of vertical distribution of SIC in arid and semi-arid land in Tunisia and its relationships with SOC, Ca^{2+} and Mg^{2+}. One of the article's contribution is the confirmation of the positive correlation between SIC and SOC in Tunisian alkaline soil. The study also showed that this correlation is stronger in high fertility soils (the oasis of Cheneni) compared to low fertility soils (the oasis of Guettaya). These findings confirm the hypothesis that the fertility and organic amendment of soil play an important role in the dynamics of SIC. They also show that SIC can equally sequester carbon, which can have a positive impact on the environment by minimizing GHGs.

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