Soil Inorganic Carbon and Climate Change in drylands? An emerging issue?

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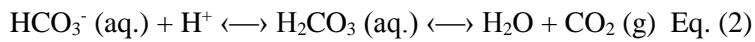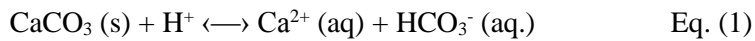[3]AgroParisTech, UMR Ecosys, Grignon FRANCE
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Introduction

Terrestrial ecosystems play a major role in regulating the concentration of CO_2 in the atmosphere. A comprehensive understanding of sinks and sources of carbon (C) and their dependence on changing climate is a highly studied research topic to produce accurate estimates of future atmospheric CO_2 concentrations. Soils are considered as one of the largest C pools on Earth. The soil C pool comprises two distinct components: soil organic carbon (SOC) and soil inorganic carbon (SIC), which roughly contribute ⅔ and ⅓, respectively. In general, more attention had been paid to the storage and dynamic of SOC pool, which is considered as a key component of soil functioning and more dynamic than SIC. Because some methodological issues persist in measuring the contribution of SOC and SIC in total soil C or CO_2 fluxes from soils, calcareous soils are poorly studied for the global C cycle. Yet, calcareous soils cover over 30% of the earth's land surface mainly in arid and semi-arid areas where an understanding of SOC dynamics is particularly critical for ensuring food security. In these regions, SOC stocks, a major determinant of soil fertility, are low and agricultural productivity is already limited by climatic conditions. Methods to separate easily SOC and SIC dynamics in soil are thus needed. A study in a large set of French soils showed the potential of mid-infrared reflectance spectroscopy (MIRS) to predict SOC and SIC contents in calcareous soils (Grinand et al. 2012). However, SIC is no more seen just as a static C pool in soils and dynamics should be studied. There is increasing evidence that equilibrium in the SIC system may be shifted in one way or another by external factors such as management practices and human-led environmental changes. The three main factors controlling dissolution and precipitation of $CaCO_3$ as listed by Gocke et al. (2011) are: (1) CO_2 partial pressure in pore space, (2) pH of soil solution, and (3) mass flow of dissolved carbon species (H_2CO_3, HCO_3^-). Biological activities and climate change can impact all of these three factors and thus may mobilize SIC to emit CO_2 or promote $CaCO_3$ precipitation by modifying the equilibrium between the different dissolved (aq.), gaseous (g) and solid (s) inorganic carbon species.

This equilibrium is formalized by the equations:

$$CaCO_3 \text{ (s)} + H^+ \longleftrightarrow Ca^{2+} \text{ (aq)} + HCO_3^- \text{ (aq.)} \qquad \text{Eq. (1)}$$

$$HCO_3^- \text{ (aq.)} + H^+ \longleftrightarrow H_2CO_3 \text{ (aq.)} \longleftrightarrow H_2O + CO_2 \text{ (g)} \quad \text{Eq. (2)}$$

Liming practices, which are aimed to increase soil pH, may stimulate CO_2 emission by carbonate dissolution (Bernoux et al. 2003). Adding plant residues or organic amendments enhances biological activities, i.e. root and microorganism respiration, resulting in an increase in CO_2 partial pressure, which may either lead to an enhanced trapping of CO_2 through carbonate precipitation, or to a decrease in soil pH resulting in the dissolution of carbonates (Gocke et al., 2011). Climate change is also likely to affect the SIC system, as the increasing atmospheric concentration of CO_2, climate warming, and variations in the amount and frequency of rainfall events could modify biological activities and thus equilibrium interactions between soil carbonates and bicarbonates (Emmerich 2003; Chevallier et al. 2016). Natural isotopic ^{13}C tracing has been performed using the difference in $\delta^{13}C$ signatures between SOC and SIC to trace the source of the CO_2 emitted from soils (Stevenon and Verburg, 2006). Here are presented two original studies: the first one in South of France to show SIC can contribute to CO_2 emissions from soil incubation in topsoils and in subsoils, the second one in Tunisia to test how temperature could affect the contributions of SOC and SIC to the CO_2 emitted from a calcareous soil.

Material and methods

French soils: Two cultivated Fluvisol with two contrasted SOC contents in topsoils, 19 and 9 g SOC kg^{-1} soil, but similar SIC content, about 64 g SIC kg^{-1} soil, were incubated for 28 days at 20°C. In subsoils (10-30, 70-100 and 160-180 cm) the SOC contents were not different between the two soils. The CO_2 and $^{13}CO_2$ emitted from soil samples were directly measured on the gas inside the incubation jars with a micro chromatographer coupled with a mass spectrometer.

Tunisian soils: A cultivated Calcari-Leptic Cambisol Tunisian topsoil (0-10 cm) which contains 66 g C kg^{-1} soil with 44 g SIC kg^{-1} soil was incubated at 4 temperatures (20, 30, 40 and 50°C) for 28 days. In order to determine its ^{13}C natural isotopic abundance, the CO_2 emitted from soil samples and trapped in NaOH was precipitated as $BaCO_3$ by adding $BaCl_2$ (20 mL, 0.5 M). The $BaCO_3$ precipitates were analysed for their carbon isotope abundance.

The contribution of SIC and of SOC to the total amount of CO_2 emitted can be calculated using the standard isotope dilution equation in a first approximation

$$\delta^{13}C_{CO2(t)} = f \cdot \delta^{13}C_{CO2\text{-}SIC} + (1-f) \cdot \delta^{13}C_{CO2\text{-}SOC}$$

This isotopic method has often been applied by implicitly assuming that the $\delta^{13}C$ of SIC-derived CO_2 ($\delta^{13}C_{CO2\text{-}SIC}$) is equal to the $\delta^{13}C$ of SIC ($\delta^{13}C_{SIC}$) and that of SOC-derived CO_2 ($\delta^{13}C_{CO2\text{-}SOC}$) is equal to the $\delta^{13}C$ of SOC ($\delta^{13}C_{SOC}$). CO_2 emission from SIC or SOC is prone to induce isotopic fractionation at various steps but we assumed that this phenomenon is limited in our case (Chevallier et al. 2016).

Results and discussion

Whatever the soils and the measurement method, alkali traps or gas analysis, the $\delta^{13}C$ signature of CO_2 emitted from soils differed significantly from that of the SOC. In French soils, the CO_2 emissions were ^{13}C-enriched by around 5‰ to 13‰ compared to the SOC and were therefore shifted towards the $\delta^{13}C$ signatures of SIC, especially at high soil depth (Fig. 1). The range of $\delta^{13}C$ signatures of gas samples did not evolve with time more than 2‰. In Tunisian soils, there are also CO_2 emissions ^{13}C-enriched compared to SOC, especially at 40 and 50°C, but this enrichment decreased dramatically with time. This high enrichment by 5 to 13‰ in ^{13}C of the total CO_2 emissions compared to the SOC was opposite to the isotopic fractionation factors predicted between SOC and CO_2 derived from SOC (e.g. Schweizer et al. 1999). Such an increase in $\delta^{13}C$ of the CO_2 emissions cannot be explained without the contribution of an external C pool with high $\delta^{13}C$. It likely signed a contribution of SIC, with $\delta^{13}C_{SIC}$ higher than $\delta^{13}C_{SOC}$, to the CO_2 emitted from soils (e.g. Stevenson and Verburg, 2006). Literature data ranged the contribution of SIC to total CO_2 emissions from 0.1 to 0.4 in dry conditions (Inglima et al., 2009). Our data showed high values from 0.15 to 0.7 especially at 40 and 50°C and in soil sampled at higher depth than 70 cm.

As expected, CO_2 emissions from soil increased with increasing temperature and are higher in topsoils than in subsoils (Fig. 2). This increase was generally attributed to a stimulation of SOC decomposition with temperature (Hamdi et al. 2013) and to a potential SOC mineralization decrease with depth as SOC contents and microbial biomass also decrease with depth (Fang and Moncrieff, 2005). There is a negative correlation between the amount of CO_2 emitted and $\delta^{13}C$ values, except at high temperature. At incubation temperature under 30°C, the SOC seems to be the main contributor to the increasing amount of evolved CO_2, even if the calculated amounts of SIC-derived CO_2 could be high in topsoils (Fig. 2). In the other hand, the low $\delta^{13}C$ values of emitted CO_2 in subsoils signed a high contribution of SIC to CO_2 (0.7) but did not represent high amounts of total emitted CO_2 from SIC (Fig. 2). The CO_2 emissions from SIC seemed to be stimulated by SOC decomposition (Fig.3). The isotope exchanges between SIC- and SOC-derived CO_2 could explain that $\delta^{13}C$ signatures of CO_2 emissions were not the equaled to the $\delta^{13}C$ signatures of the SOC. The dynamics of SOC and SIC can be closely linked according to the equation:

$$H_2O + CO_2 + CaCO_3 \text{ (s)} \longleftrightarrow Ca^{2+} \text{ (aq)} + 2HCO_3^- \text{ (aq.)} \quad \text{Eq. (3)}$$
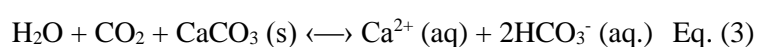
This equation illustrates the possible exchange pathways of C between SOC-derived CO_2 and SIC-derived bicarbonate. In such a scheme, going back and forth, CO_2 emitted by SOC can replace and

displace SIC carbonate, which would generate "SIC-labelled" CO_2. The SOC-derived CO_2 is likely to be the essential factor in the dissolution of SIC in the absence of additional H^+ sources. The CO_2 emissions would also be labeled SIC even though they were entirely dependent on SOC mineralization. In other words, an increase in the SIC signature of emitted CO_2 does not directly imply an additional contribution of SIC as a source of CO_2.

At high temperatures, other equilibrium seems to occur. The CO_2 emissions from SIC seemed to be stimulated by additional mechanism than solely SOC decomposition (Fig.3). The increase in CO_2 emissions came along with an increase of the $\delta^{13}C$ signature of the emitted CO_2. The CO_2 emissions from SIC seemed to be stimulated by temperature. A higher dissolution of SIC is not the explanation as solubility of CO_2 in water decreases with increasing temperature. Isotopic fractionation factors between SIC and SIC-derived CO_2 are temperature dependent, being greatest at low temperatures (Bottinga, 1969). This could explain a part of the increase in $\delta^{13}C$ emitted CO_2 without the need for invoking a higher amount of CO_2 from SIC with temperature.

Although the qualitative SIC contribution to emitted CO_2 from soils incubated in lab suffers low doubt, this study confirms that quantitative appraisal and assignment are far from being straight forward. Increasing soil temperatures seem to modify dramatically the apparent SIC dynamics. Due to the complexity and diversity of involved phenomena additional information is needed to unravel the mechanisms underlying the effects of temperature on quantity and signature of emitted CO_2.
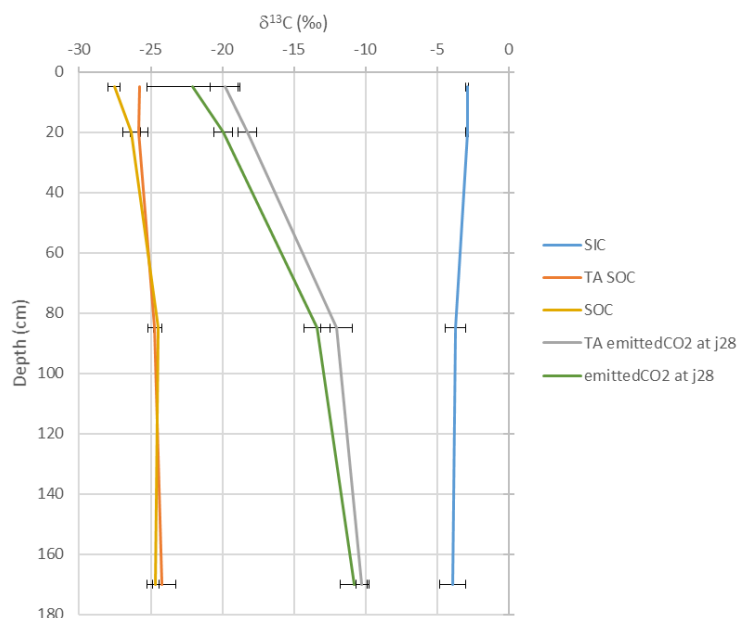
Fig. 1 $\delta^{13}C$ (‰) profil of SOC and SIC and the CO_2 emitted from 2 soils with similar SIC contents but different SOC contents after 28 days (21-28 days).
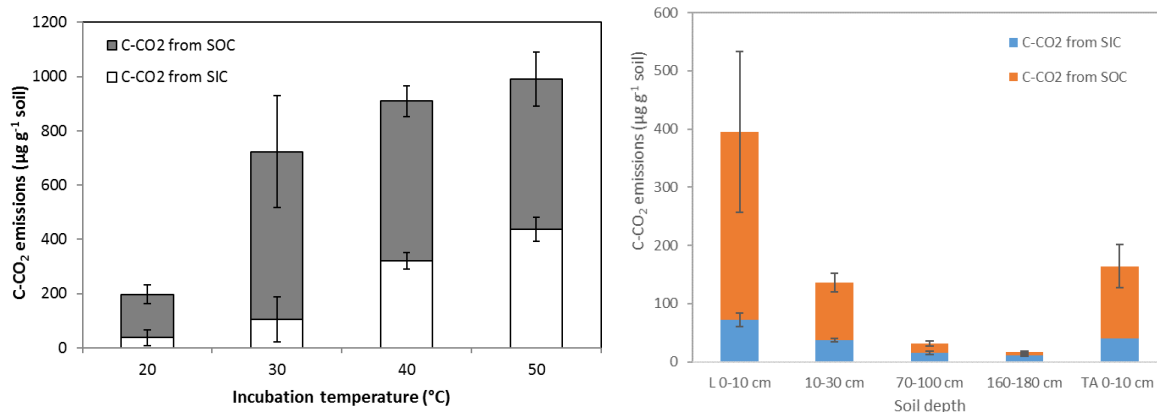
Fig. 2 Cumulative C-CO$_2$ emissions from soil organic carbon (SOC) and from soil inorganic carbon (SIC) during 28 days of incubations at different temperatures and soil depth. L 0-10 cm and TA 0-10 cm are two top soils with similar SIC contents but different SOC contents.
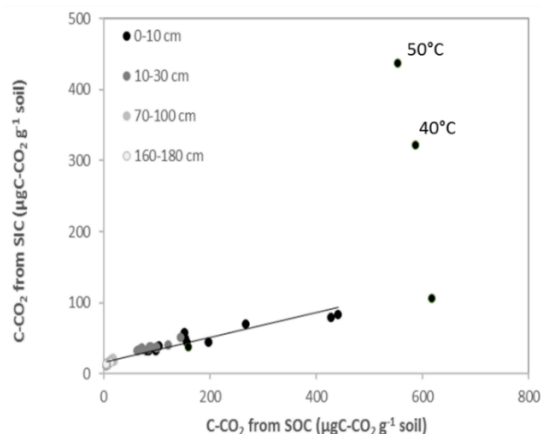
Fig. 3 Relationship between cumulated CO$_2$ from SIC and SOC of all the soils sampled after 28 days of incubation.

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