



Temperature dependence of CO₂ emissions rates and isotopic signature from a calcareous soil



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ABSTRACT

In the context of climate change, studies have focused on the temperature dependence of soil CO₂ emissions. Although calcareous soils cover over 30% of the earth's land surface, few studies have considered calcareous soils where soil inorganic carbon (SIC) makes the analysis of the C fluxes at the soil to air interface more complex.

This study tested how temperature could affect the contributions of soil organic carbon (SOC) and SIC to the CO₂ emitted from a calcareous soil. The soil pH, CO₂ emissions and δ¹³C signatures of CO₂ were measured after soil incubations at 4 temperatures (20 °C, 30 °C, 40 °C and 50 °C).

The CO₂ emissions and the δ¹³C signature of the emitted CO₂ increased with temperature. The proportion of SIC-derived CO₂ in these emissions seemed to be stimulated by temperature.

Three processes were discussed: (1) isotopic fractionations, (2) temperature impacts on SIC- and SOC-derived CO₂, and (3) isotope exchanges between SIC- and SOC-derived CO₂. The use of δ¹³C signature analysis to determine the contribution of SIC and SOC to the total CO₂ emissions from soil is not straightforward. An increase in the SIC signature of emitted CO₂ does not directly imply an increase in SIC as a source of CO₂.

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1. Introduction

Terrestrial ecosystems play a major role in regulating the concentration of CO₂ in the atmosphere. A comprehensive understanding of sinks and sources of carbon (C) and their dependence on changing temperature is required to produce accurate estimates of future atmospheric CO₂ concentrations (Lapenis et al., 2008). Soil organic carbon (SOC) decomposition is one of the major fluxes and estimates range from 50 to 75 Pg C yr⁻¹ (Raich and Schlesinger, 1992; Schimel, 1995; IPCC, 2007). Even relatively small changes in this source may have a significant effect on the atmospheric CO₂ concentration. Recent studies have focused on understanding the temperature dependence of the soil microbial activities involved in SOC decomposition but all processes involved in the temperature

dependence of SOC decomposition needs to be more clearly understood (Davidson and Janssens, 2006; Kirschbaum, 2006).

An understanding of soil carbon dynamics is also particularly critical in drylands, arid and semi-arid regions, 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 (Romanyà and Rovira, 2011). However little research has been carried out into drylands for several reasons, in particular because the presence of soil inorganic C (SIC) from calcareous stone may affect the analysis of the C fluxes at the soil to air interface (Tamir et al., 2011, 2012). Although calcareous soils cover over 30% of the earth's land surface (Chen and Barak, 1982; Stevenson and Verburg, 2006; Yang et al., 2010; Romanyà and Rovira, 2011) and the global SIC pool has been estimated to be in the range 700–950 Pg C (Batjes, 1996; Romanyà and Rovira, 2011), it is not yet clear how and under what conditions this large inorganic pool may be affected by changing climatic conditions. Studies on the positive or negative effect of irrigation or rain events on the

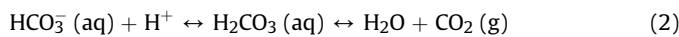
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¹ In memoriam.

contribution of carbonates to the CO₂ emissions from dryland soils are conflicting (Emmerich, 2003; Serrano-Ortiz et al., 2010) and no study has considered the impact of soil temperature on CO₂ emission from calcareous soils in drylands soils, where heat waves are expected to become more frequent and extreme within the 21st Century (IPCC, 2007).

The three main factors controlling dissolution and precipitation of CaCO₃ as listed by Gocke et al. (2011) are: (1) CO₂ partial pressure in pore space, (2) pH of soil solution, and (3) mass flow of dissolved carbon species (H₂CO₃, HCO₃⁻). The increase of temperature impacts the SOC decomposition and modifies all of these three factors and thus may mobilize SIC to emit CO₂. Indeed the increase of temperature might modify the equilibrium between the different dissolved (aq.), gaseous (g) and solid (s) inorganic carbon species. This equilibrium is formalized by the equations:



Some authors have suggested that inputs of hydrogen ions, organic acids, or other biological pH-active reactions such as nitrification from decomposing organic matter, probably dissolve carbonate and stimulate CO₂ emission (Emmerich, 2003; Stevenson and Verburg, 2006; Bertrand et al., 2007; Tamir et al., 2012). Other authors have suggested that biological activities, such as microorganism respiration and consequent increase in CO₂ partial pressure in pore space or such as ammonification which can cause a pH increase, can result in carbonate precipitation (Gocke et al., 2011).

The objectives of the study were to quantify (i) the impact of increasing temperature on CO₂ emissions from a calcareous soil, (ii) the impact of increasing temperature on the contribution of SOC and SIC to these CO₂ emissions from soil. This study was, therefore, designed to quantify the pH evolution and the relative contributions of SOC and SIC sources to the amount of CO₂ emitted by a calcareous agricultural soil at 4 different incubation temperatures (20 °C, 30 °C, 40 °C and 50 °C). Natural isotopic ¹³C tracing was performed using the difference in δ¹³C signatures between SOC and SIC to trace the source of the CO₂ emitted (Stevenson and Verburg, 2006; Bertrand et al., 2007; Tamir et al., 2012).

This isotopic method used to trace CO₂ from calcareous soils has often been applied by implicitly assuming that the δ¹³C of SIC-derived CO₂ (δ¹³C_{CO₂-SIC}) is equal to the δ¹³C of SIC (δ¹³C_{SIC}) and that of SOC-derived CO₂ (δ¹³C_{CO₂-SOC}) is equal to the δ¹³C of SOC (δ¹³C_{SOC}). However isotopic fractionations occur during all reactions leading to CO₂ emissions. Isotopic fractionation factors of CO₂ emitted by SIC have been determined experimentally in many articles reviewed by Skidmore et al. (2004); δ¹³C_{CO₂-SIC} is more negative by 7‰–9‰ compared to δ¹³C_{SIC} in field conditions. These isotopic fractionation factors are temperature dependent, being greatest at low temperatures (Bottinga, 1969; Deines et al., 1974; Szaran, 1997). Regarding CO₂ emissions from SOC, the use of ¹²C rather than ¹³C by decomposers could also reduce the ¹³C in the SOC-derived CO₂. Indeed, slight decreases (with amplitudes ranging from 1‰ to 3‰) in δ¹³C of emitted CO₂ compared to the δ¹³C of SOC were recorded (Schweizer et al., 1999; Andrews et al., 2000). However some studies showed no indication of isotopic fractionation during the SOC decomposition (Cheng, 1996; Boström et al., 2007). This isotopic fractionation factor during SOC decomposition seems to depend on the incubation time and the chemical nature of the organic substrates, but no temperature dependence was detected between 22 and 40 °C (Andrews et al., 2000). Should the calculation of the contribution of SIC and SOC in the total amount of CO₂ emissions from calcareous soils take these isotopic fractionation factors into account? This paper discusses about this

methodological issue in testing both calculations (1) taking isotopic fractionation into account for estimating SIC contribution to CO₂ emissions and (2) not taking isotopic fractionation into account as performed by Bertrand et al. (2007) and Tamir et al. (2012).

We hypothesized that the δ¹³C_{CO₂} of the CO₂ emissions from calcareous soil is temperature dependent and consequently that both SIC and SOC-derived CO₂ emissions are sensitive to temperature. Thus, we performed an analysis of CO₂ emissions amount and signatures at different temperatures. The aim was to test whether SIC- and SOC- derived CO₂ emissions show similar or different patterns in terms of temperature dependency.

2. Materials and methods

2.1. Soil samples description

Soil samples (2 kg) were taken from the upper layer (0–10 cm) of five field replicates at the experimental station of Sidi Ahmed Essaleh in North-West Tunisia (35°43'N; 8°35'E; alt. 621 m). The plots had been under a durum wheat/forage sorghum rotation for the past 50 years. The soil was a reddish brown Calcari-Leptic Cambisol as defined in the FAO/UNESCO classification. It was silty clay (36% clay, 50% silt, 14% sand) with 66.3 g total C kg⁻¹, 1.4 g total N kg⁻¹ and a pH of 8.9. This high soil pH value was in the range of the pH values, from 4.9 to 9.6 with median at 8.1, measured in superficial horizons in Tunisian soils (Brahim et al., 2012). The SIC was 44.2 g CaCO₃-C kg⁻¹soil, i.e. 66.7 ± 1.4% of total soil C was in the form of calcium carbonates. The mean annual temperature was 16.3 °C and the mean monthly temperature ranged from 7.8 °C in January to 26.5 °C in August, with a maximum temperature up to 47 °C. The mean annual precipitation was 469 mm (Climatic data over the period 1951–2004, National Institute of Meteorology in Tunisia).

2.2. Incubation, analyses and statistics

Moist soil samples (around 10 g H₂O 100 g⁻¹ dry soil) were sieved to remove coarse plant debris (>3 mm) and stored for three months in a cold room (<4 °C) before incubation (Hamdi et al., 2011). Before incubation, water was added to each soil sample to reach a water potential of –0.01 MPa determined with a 3 bar pressure plate. All moist soil samples (around 18 g H₂O 100 g⁻¹ dry soil) were then kept for 1 week at 20 °C to allow microbial activity to resume (Creamer et al., 2014) and to avoid to measure the initial flush of mineralization induced by soil re-wetting. As the CO₂ flush after soil re-wetting does not last more than 5 days (Fierer and Schimel, 2002; Yemadje et al., 2016), the period of CO₂ production measurement would not contain this flush.

Subsamples of 15 g from each soil sample were incubated at four different temperatures (20 °C, 30 °C, 40 °C and 50 °C) for 28 days. High temperatures were specially chosen to mimic impact of heat wave events (in the region from which the soils originate, temperature can reach 47 °C on summer, according to records from Tunisian National Institute of Meteorology). Each 15 g subsample was placed in a 1 L airtight jar with a vial of Milli-Q water (20 mL) to avoid soil drying, and a vial containing 20 mL aqueous NaOH solution (0.5 M) to trap the CO₂ emitted (Hamdi et al., 2011). Water content was checked to remain constant by weekly weighing. Each time the jars were opened to check soil moisture, NaOH traps were closed to avoid contamination by atmospheric CO₂. Five jars without soils but with NaOH traps were also incubated at each temperature to determine amount and isotopic content of initial atmospheric CO₂. The amounts of emitted C were measured by removing the NaOH CO₂ trap and analyzing the dissolved C on days 7 and 28. The CO₂ trapped in the NaOH solution was measured by

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