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On the apparent CO_2 absorption by alkaline soils

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Abstract

Alkaline soils in the Gubantonggut Desert were recently demonstrated socking away large quantities of CO_2 in an abiotic form. This demands a better understanding of abiotic CO_2 exchange in alkaline sites. Reaction of CO_2 with the moisture or dew in the soil was conjectured as a potential mechanism. The main goal of this study is to determine the extent to which the dew deposition modulates Land–Atmosphere CO_2 exchange at highly alkaline sites (pH ~ 10). Experiments were conducted at the most barren sites (canopy coverage < 5 %) to cut down uncertainty. Dew quantities and soil CO_2 fluxes were measured using a micro-lysimeters and an automated flux system (LI-COR, Lincoln, Nebraska, USA), respectively. There is an evident increase of dew deposition in nocturnal colder temperatures and decrease in diurnal warmer temperatures. Variations of soil CO_2 flux are almost contrary, but the increase in diurnal warmer temperatures is obscure. It was shown that the accumulation and evaporation of dew in the soil motivates the apparent absorption and release of CO_2. It was demonstrated that dew amounts in the soil has an exponential relation with the part in F_c beyond explanations of the worldwide utilized Q_{10} model. Therefore dew deposition in highly alkaline soils exerted a potential CO_2 sink and can partly explain the apparent CO_2 absorption. This implied a crucial component in the net ecosystem carbon balance (NECB) at alkaline sites which occupies approximately 5 % of the Earth's land surface (7 million km). Further explorations for its mechanisms and representativeness over other arid climate systems have comprehensive perspectives in the quaternary research.

1 Introduction

After the Industrial Revolution, the world's concerned scientific community made a huge effort to investigate sources and sinks in the global carbon cycle, which revealed that the global CO_2 budget cannot be balanced unless invoking a missing sink (Detwiler

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et al., 1988; Tans et al., 1990). Soil CO_2 flux (F_c) accounts for 20–38 % of the annual, global terrestrial and marine CO_2 emissions into the atmosphere and is a crucial modulator for ongoing anthropogenic perturbations to the natural carbon cycle (Raich et al., 1992). In most publications, F_c was primarily attributed to the root and microbial respiratory components (Billings et al., 1998; Holt et al., 1990; Reth et al., 2005). However, soil abiotic CO_2 exchange was recently recommended to explain some mysterious CO_2 fluxes measured over the carbonate ecosystems (Emmerich, 2003; Fang et al., 2001; Kowalski et al., 2008). Although further investigations are still required to determine whether these mysterious CO_2 fluxes are "anomalous" or representative (Schlesinger et al., 2009), they can temporally dominate the net ecosystem carbon balance (NECB) (Serrano-Ortiz et al., 2010; Sanchez-Cañete et al., 2011; Kowalski et al., 2008; Inglima et al., 2009) and implies a hidden carbon cycle loop potentially contributing to the long-sought missing sink (Stone, 2008).

Especially, the measurements of F_c in the Gubantonggut Desert demonstrated that alkaline soils are socking away large quantities of CO_2 in an abiotic form (Stone, 2008; Xie et al., 2009). This demands a better understanding of abiotic CO_2 exchange in alkaline soils. Further studies demonstrated that the soil abiotic CO_2 exchange has a significant implication to the diel pattern of F_c (Chen et al., 2013). Despite of its little-known soil mechanism, it has been further demonstrated by measurements at alkaline sites over other arid regions and ecosystems (Yates et al., 2013), implying that the extent to which alkaline soil modulates carbon dynamics on regional and global scales was inadequately studied and poorly understood. Alkaline soils occupy approximately 5 % of the Earth's land surface (7 million km), and will increase due to the global trend towards increasing desertification (Xie et al., 2009). So it is significant to identify the determining environmental factors of F_c in alkaline soils and address its response to the simultaneously varying physical and biotic factors (Ball et al., 2009).

In speculation from soil chemists, reaction of CO_2 with the moisture or dew in the soil was recommended as a potential mechanism (Stone et al., 2008). This scenario is plausible. It might explain the story for apparent CO_2 absorption by alkaline soils at summer night, when CO_2 can react with moisture in the soil and perhaps with dew to form carbonic acid, which in turn dissolves calcium carbonate (unlike most minerals, carbonates become more soluble at lower temperatures). It must be noted that diurnal warmer temperatures would drive a reverse reaction and release the CO_2 again during the night. It is still undetermined whether the accumulation of dew in the soil can motivate the apparent absorption of CO_2. To make things worse, the dew deposition in alkaline soils would vary from season to season, implying no significant increase in soil storage due to this process over a year.

Nevertheless, the conjecture is intriguing and must be followed up. In arid and semi-arid areas, apart from precipitation in the form of rain or snow, dew plays a vital role in providing an essential source of water for alkaline soils. Especially in desert ecosystems, the water resources are severely limited and dewfall and early morning evaporation are the most important processes affecting the daily water balance of the upper soil layer (Ball et al., 2009; Broza, 1979; Duvdevani, 1964; Jacobs et al., 1999; Moffett, 1985). High efficiency in water use and simultaneous annual carbon gain in the Gubantonggut Desert has been demonstrated (Zhang et al., 2009; Liu et al., 2012). Even if the reaction of CO_2 with the moisture or dew in alkaline soils were negligible, the significant dew deposition might exert a potential CO_2 sink and partly explain apparent CO_2 absorption frequently occurs in nighttime flux measurements (Xie et al., 2009; Yates et al., 2013).

The objectives of this research are to present the details in the variations of F_c with dew accumulation and evaporation in alkaline soils, and in turn, to achieve a better understanding of the relationship between dew deposition and apparent CO_2 absorption in alkaline soils. Diel variations of dew amounts with air temperature at 10 cm above the soil surface were determined. Measurements of F_c at highly alkaline sites (pH ~ 10) were conducted along a gradient of dew amounts. This might present a better understanding of the extent to which dew deposition modulates the Land–Atmosphere CO_2 exchange at highly alkaline sites and the possible implications to the net ecosystem carbon balance (NECB).

2 Materials and methods

I claim that all the experiments in the study were conducted at the Gubantonggut Desert. I confirmed that no specific permissions were required for this research, and exactly, the local government encouraged us to do so since it improved the environment. No endangered or protected species were involved in the field studies.

2.1 Site description

The considered highly alkaline sites are from an arid climate system in the southern periphery at the Gubantonggut Desert, which is located at the hinterland of the Eurasian Continent. Soils are clay-loam of a texture with heavy alkalinity. Because of extremely arid meteorological conditions (annual sunshine hour: 3079 h; annual precipitation: 144.7 mm; annual evapotranspiration: 2020 mm; annual Rad intensity: 5439 MJ m^{-2}; annual mean wind velocity: 2.6 $m\,s^{-1}$), dew deposition is an essential source of water and the nighttime vapor uptake by alkaline soils is evident during the arid growing seasons (Zhang et al., 2009). To highlight the role of the abiotic components in F_c, the most barren sites (canopy coverage $< 5\,\%$) were chosen for our case study. There is no significant difference in the geochemical properties between sites. To cut down uncertainty, only bare, highly alkaline sites (pH ~ 10) far from the sparse vegetation were considered. All the experiments in the study were conducted at the Gubantonggut Desert. No specific permissions were required for this research, and exactly, the local government encouraged us to do so since it improved the environment. No endangered or protected species were involved in the field studies.

2.2 Soil CO_2 flux measurements

Measurements of F_c were conducted during an arid growing season of 2006, using an LI-8100 Automated Soil CO_2 Flux System (LI-COR, Lincoln, Nebraska, USA), equipped with a long-term monitoring chamber (LI-8100L). Before experiments, litter on the soil surface was cleared. In order to minimize the disturbing effect on the soil, at least 48 h before measurements of F_c, steel collars (ca. 20.3 cm in diameter and 19.5 cm in depth) were inserted into the soil, with a 5 cm exposed above the surface for installing the monitoring chamber. Each measurement was commenced at 06:00 and ended at 06:00 LT on the next day. During measuring period, F_c value was documented for every 15 min and each measurement length was 2 min. Air temperature 10 cm above the surface (T_{as}) and relative humidity (RH) were monitored automatically by the corresponding probes equipped with LI-8100 System. To exclude the influence of rainfall, all the observations were conducted in clear days and the collars were covered when raining.

2.3 Dew quantities measurements

Measurements of dewfall and evaporation were conducted in growing seasons of 2008, using micro-lysimeters (ca. 6 cm in diameter and 3.5 cm in depth), which allows repeated use of the same sample since a soil core can be taken while leaving the surface intact (Boast et al., 1982). The micro-lysimeters were pushed into the ground to collect undisturbed soil columns for control with the edges close to the flat surface of the ground and the bases covered. There were 12 plots (1 m × 1 m) were taken from each plot at every time. Soil samples were weighted using a balance to a precision of ±0.01 g. Dew amounts was determined by calculating the weight difference. The weighing intervals are 2 h and 30 min for the time course of the dew deposition and dew duration respectively. A hygrothermograph (HC-520) is employed to measure T_{as} and RH synchronously.

2.4 Procedure for sensitivity analysis

Motivated by the speculation from soil chemists (Stone, 2008), a preliminary analysis were executed to investigate whether the temporal variations of F_c are similar to that of dew amounts in the soil. Following preparation from November 2010 to March 2011 (a long-term incubation of roots-excluded soils in dry environments to depress the respiratory components in the soil and focus on the implications of dew amounts to soil abiotic CO_2 exchange), the further laboratory studies were commenced in August 2012 to observe the variations of F_c with the evaporation and accumulation of dew. An ultimate analysis was conducted to investigate the extent to which dew deposition modulator the part in F_c beyond explanations of the worldwide utilized Q_{10} model (Lloyd et al., 1994), using a developed Q_{10} model as

$$F_c = R_{10}Q_{10}^{(T-10)/10} + F_x \tag{1}$$

where F_x is the part in F_c beyond explanations of the Q_{10} model, $T = T_{as}$, R_{10} is the referred F_c at 10° and Q_{10} is the factor by which F_c is multiplied when T increases by 10°.

For the model parameterization, first we determined R_{10}, Q_{10} by taking F_x as a constant parameter, and then calculated F_x by $F_x = F_c - R_{10}Q_{10}^{(T-10)/10}$. The sensitivity of F_c to dew deposition was analyzed by an exponential model as

$$F_x = a\,e^{\lambda \mathrm{dew}} + b \tag{2}$$

3 Results

3.1 Variations of dew amounts and soil CO_2 flux

The dew amounts in four sampled soils indicated no significant spatial difference of dew accumulation and evaporation at highly alkaline sites (Fig. 1). The magnitude of dew amounts in the soil varied largely with a range between some $-0.02 \sim 0.08$ mm. Dew accumulations in the measuring period were begun at 20:00 and ended at 08:00 LT on the next day, while dew evaporations were begun at 09:00 and ended at 19:00 LT. Negative dew values implied that dew evaporations in the whole diel cycle were stronger than dew depositions because of the arid climate. There is an evident increase of dew deposition in nocturnal colder temperatures and evident decrease in diurnal warmer temperatures. Dew amounts, nocturnal colder temperatures, and profile storage of soil inorganic carbon (Wang et al., 2010) implies the possible nighttime accumulations of pedogenic inorganic carbon (PIC) with dew deposition at the considered alkaline sites, which are controlled by the carbonate–bicarbonate equilibria (Eqs. 3 and 4) (Emmerich, 2003):

$$CO_2 + H_2O \leftrightharpoons HCO_3^- + H^+ \tag{3}$$

$$CaCO_3 + H^+ \leftrightharpoons Ca^{2+} + HCO_3^- \tag{4}$$

On the clear days within a growing season of 2006, variations of F_c are almost contrary to those of dew amounts, but the increase in diurnal warmer temperatures became obscure, implying reduced temperature sensitivity of diurnal CO_2 fluxes (Fig. 2). This might be attributed to the undetermined but significant time lag between the "apparent" respiration (F_c) and real respiration (R_s) (Fang et al., 1999). The intensity of F_c varied largely with a range between some $-1.2 \sim 1.2\,\mu mol\,m^{-2}\,s^{-1}$. Nocturnal negative values of F_c indicated an evident apparent absorption of CO_2 in highly alkaline soils, which could be partly attributed to the above well-known chemical reactions.

3.2 Sensitivity of F_c to dew deposition

Laboratory temperature-controlled experiments revealed that intensity of F_c definitely decreases with dew accumulation to the soil at colder air temperatures (Fig. 3), with the intensity of F_c varied largely with a range between some $-2 \sim 0.7\,\mu mol\,m^{-2}\,s^{-1}$. About 85 % of measured F_c were negative and indicated apparent CO_2 absorption. But dew evaporation from the soil at warmer air temperatures drives F_c in the opposite direction (Fig. 4), where the intensity of F_c varied from $-1\,\mu mol\,m^{-2}\,s^{-1}$ to $2.5\,\mu mol\,m^{-2}\,s^{-1}$. About 78 % of measured F_c were positive and indicated apparent CO_2 release. Therefore the dew accumulation and evaporation in the soil are closely related to the apparent CO_2 absorption (negative F_c) and the apparent CO_2 release (positive F_c).

Estimations of F_c with Eq. (1) along a field temperature gradient were still robust and it explains more than 86 % of the data (Fig. 3: $R^2 = 0.8630$, RMSE = 0.2334), although F_c varied with a wide range ($-1.2 \sim 3.6\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$). Determined R_{10}, Q_{10} (taking F_x as a constant c) shown that high alkalinity significantly affected soil microbial activity and the rate of soil C cycling ($R_{10} > 2.5$) and reduced the temperature sensitivity ($Q_{10} < 1.2$). Field estimations of F_c with Eq. (1) also revealed a non-negligible CO_2 sink ($c = -2.86$).

The calculated F_x in the soil with negligible dew amounts (< 0.05 mm) varied from $-1.5\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$ and $0.1\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$, while the calculated F_x with significant dew deposition (> 0.05 mm) varied largely with a range between some $-7 \sim -1\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$. There is an evident decrease of F_x with increasing dew amounts. The robustness in the analysis of F_x with Eq. (2) was also influenced by dew amounts. It was not robust for negligible dew amounts (b: $R^2 = 0.1008$, RMSE = 0.4219). But it was robust otherwise (c: $R^2 = 0.5264$, RMSE = 0.7533).

It was demonstrated that dew amounts in the soil has an exponential relation with the part in F_c beyond explanations of the worldwide utilized Q_{10} model. Coupled with the relevance between the dew accumulation/evaporation in the soil and the apparent CO_2 absorption/release, we concluded that dew deposition in highly alkaline soils exerted a potential CO_2 sink and can partly explain the apparent CO_2 absorption.

3.3 Implications and Outstanding issues

There are numerous studies concerned the behavior of CO_2 fluxes over high-carbonate soils implying possible abiotic CO_2 exchange in desert ecosystems. Acid rain events were associated with apparent CO_2 absorption due to carbonate dissolution (Emmerich, 2003; Kowalski, 2008). And later, when the soil profile dried, the loss of water from the soil solution caused CO_2 release (Emmerich, 2003). Other concordant studies also concluded that an abiotic CO_2 source (dissolution of carbonates) provoke a portion of the measured CO_2 emissions (Wohlfahrt et al., 2008). Abiotic exchange can temporally dominate the net CO_2 exchanges of carbonate soils with the atmosphere, according to the large CO_2 release during the dry seasons in two carbonate ecosystems and weathering processes (dissolution and precipitation of carbonates) were suggested interpreting anomalous CO_2 fluxes over carbonate ecosystems (Kowalski et al., 2008).

Although the true mechanisms are still in debate (Schlesinger et al., 2009), soil abiotic CO_2 exchange may be significant in the global carbon cycle and could even represent the long-sought missing carbon sink (Stone, 2008). High contributions of soil inorganic carbon release (40 % of the total soil CO_2 efflux) during dry soil conditions in a carbonate Mediterranean ecosystem have been demonstrated (Inglima et al., 2009). Large magnitudes of CO_2 uptake were observed from soil chambers in the Gubantonggut Desert and highlighted that deserts are unsung players in the carbon cycle (Stone, 2008; Xie et al., 2009). Estimated NECB for a Mojave Desert grassland ecosystem exceeds $100\,\mathrm{g\,m^{-2}\,yr^{-1}}$, which are similar to that of some temperate forests (Wohlfahrt et al., 2008). It was originally attributed to the expansion and growth of cryptobiotic crust organisms (Wohlfahrt et al., 2008), but other scientists pointed out that these crust species are neither sufficiently active nor extensive to explain such a magnitude of CO_2 uptake (Stone, 2008). Certainly, the large CO_2 uptake is also beyond of explanation by weathering processes and subterranean cavities as a temporal depot of CO_2, along with their seasonal ventilation were hypothesized as further abiotic mechanisms (Serrano-Ortiz et al., 2010).

The present study suggested that dew amounts was a crucial modulator for the Land–Atmosphere CO_2 exchange in highly alkaline soils (pH ∼ 10) at the most barren sites (canopy coverage < 5 %). Accumulation and evaporation of dew in the soil were demonstrated to be a sensitive modulator for the apparent CO_2 absorption and release at desert alkaline soils. Interpretations of soil abiotic CO_2 exchange observed over the considered desert system might be not too easy for quite understanding. But profile storage of soil inorganic carbon revealed high carbonate content of alkaline soils at the same desert (Wang et al., 2010) and soil CO_2 flux measurements demonstrated the significance of abiotic CO_2 exchange in typical alkaline sites at this desert (Xie et al., 2009).

Nevertheless, the underlie mechanisms for dew deposition to modulator CO_2 flux in highly alkaline soils are complex and undetermined. Moreover, we cannot claim its representativeness over other arid climate systems or even for other alkaline soils ($pH < 10$) in the considered desert ecosystems. Further explorations are hence required.

4 Conclusions

Dew evaporation and accumulation have potential influence on CO_2 fluxes in highly alkaline soil. As an environmental factor that simultaneously varies with temperature, it might be partly responsible for the reduced temperature sensitivity. Dew amounts in the soil have an exponential relation with the part in F_c beyond explanations of the worldwide utilized Q_{10} model. The extent to which the dew deposition modulates Land–Atmosphere CO_2 exchange in alkaline soils was inadequately studied and poorly understood. Dew deposition in highly alkaline soils exerts a potential CO_2 sink and can partly explain the apparent CO_2 absorption. This implied a crucial component in the net ecosystem carbon balance (NECB) at alkaline sites which occupies approximately 5 % of the Earth's land surface (7 million km) and has comprehensive perspectives in the quaternary research.

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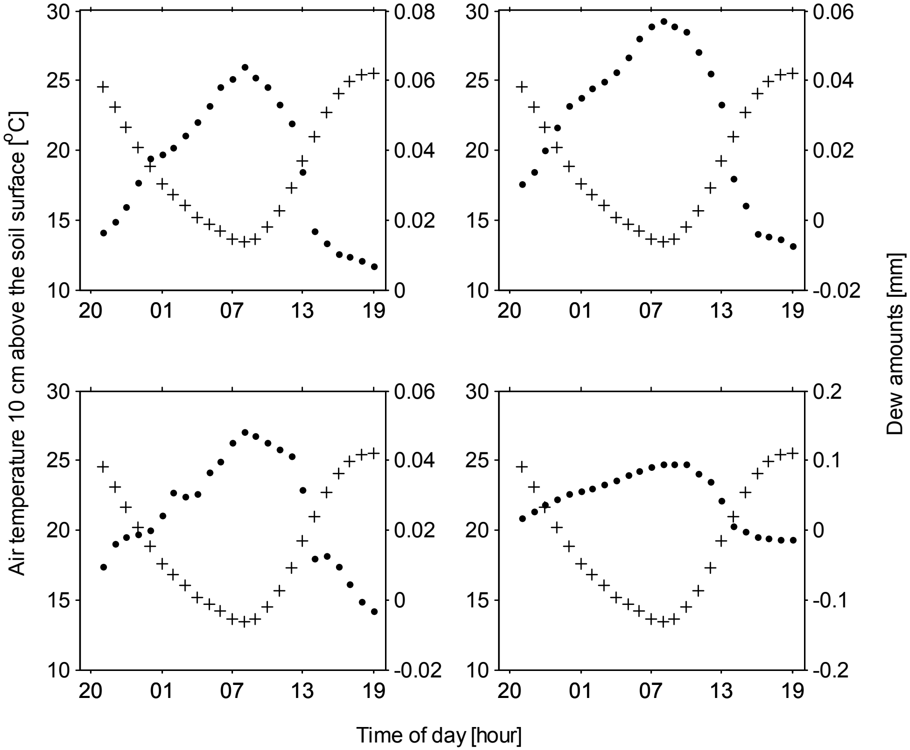

Fig. 1. Diurnal and nocturnal variations of dew evaporation and accumulation (•) in four soil samples and the simultaneous variations of air temperature 10 cm above the soil surface (+).

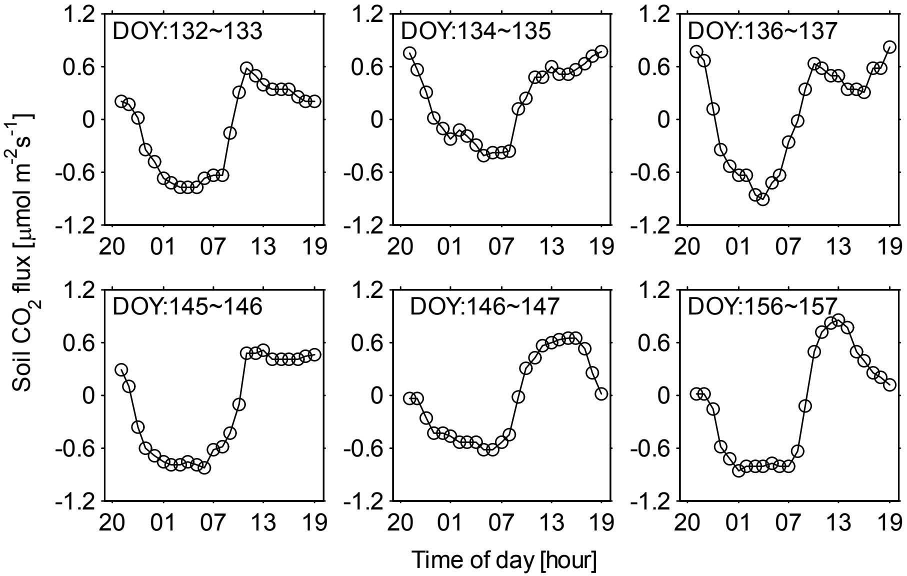

Fig. 2. Diurnal and nocturnal variations of CO_2 flux in highly alkaline soils on clear days within a growing season of 2006.

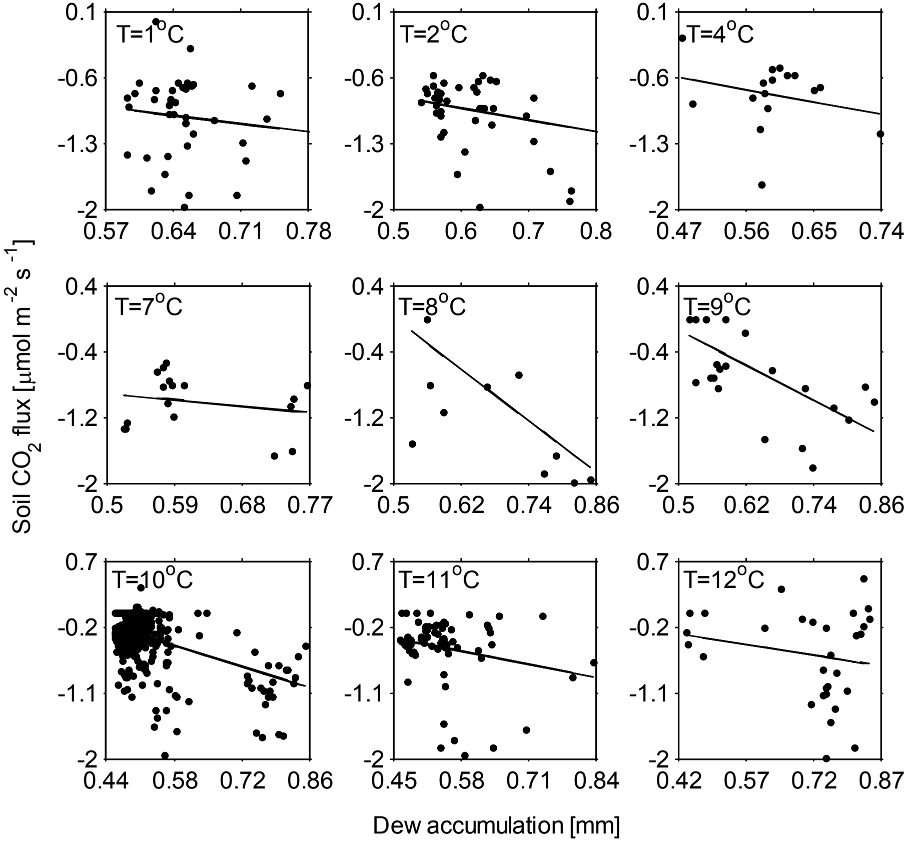

Fig. 3. Variations of soil CO_2 flux with dew accumulation along a laboratory gradient of colder air temperatures (*T*).

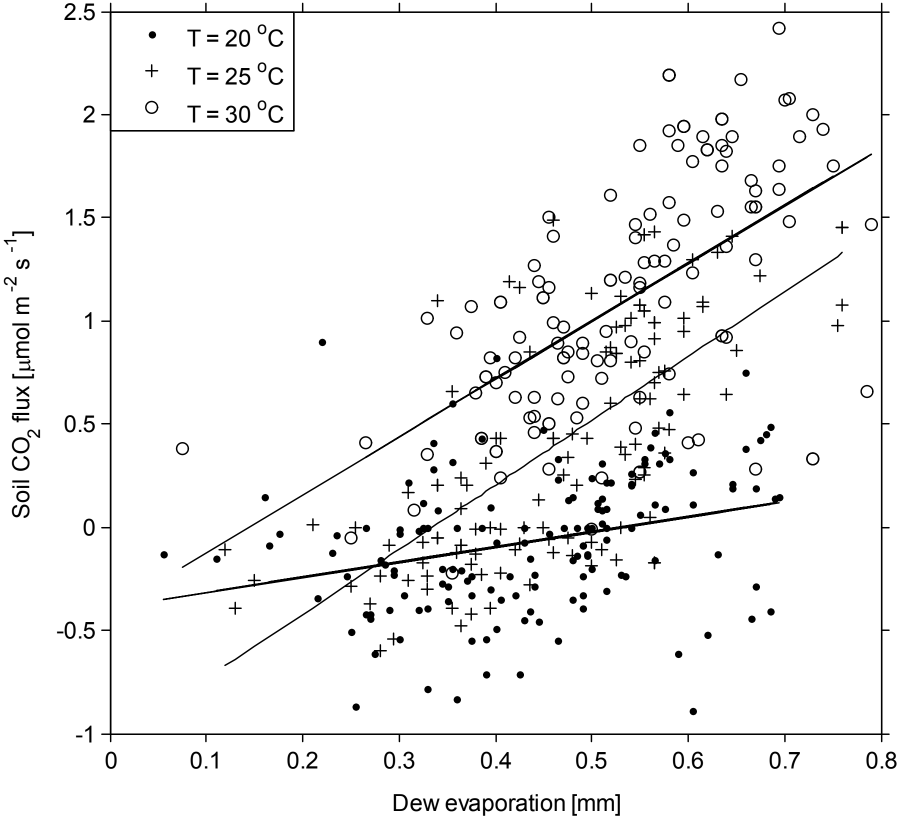

Fig. 4. Variations of soil CO_2 flux with dew evaporation along a laboratory gradient of warmer air temperatures (T).

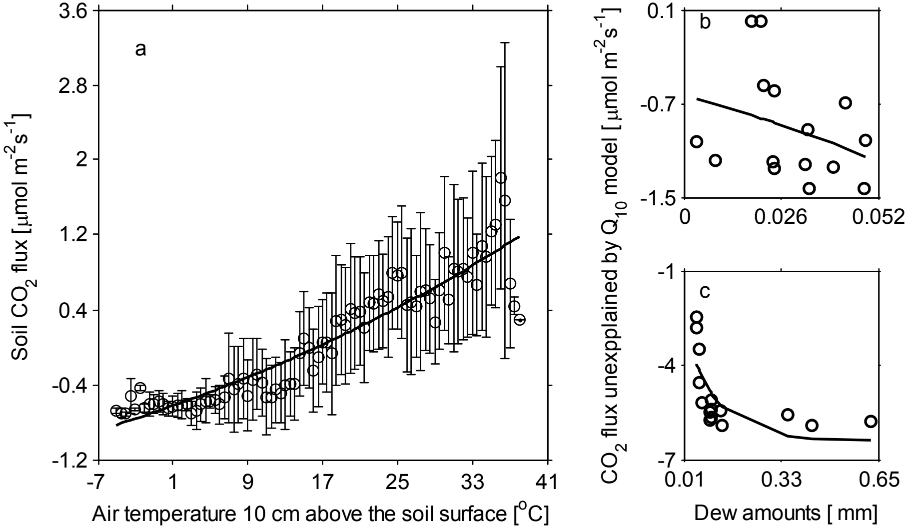

Fig. 5. Estimation of soil CO_2 flux (F_c) with $F_c = 2.58 \times 1.17^{(T-10)/10} - 2.86$ along a field gradient of T (a: $R^2 = 0.8630$, RMSE = 0.2334), and analysis of the contributions of dew amounts in F_x with $F_x = -0.82 \times e^{10 \times \mathrm{dew}} + 0.18$ (b: $R^2 = 0.1008$, RMSE = 0.4219) and $F_x = 4.07 \times e^{-10 \times \mathrm{dew}} - 6.38$ (c: $R^2 = 0.5264$, RMSE = 0.7533), where F_x is defined as CO_2 flux unexplained by the Q_{10} model.