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An inorganic CO₂ diffusion and dissolution process explains negative CO₂ fluxes in saline/alkaline soils

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An ‘anomalous’ negative flux, in which carbon dioxide (CO₂) enters rather than is released from the ground, was studied in a saline/alkaline soil. Soil sterilization disclosed an inorganic process of CO₂ dissolution into (during the night) and out of (during the day) the soil solution, driven by variation in soil temperature. Experimental and modeling analysis revealed that pH and soil moisture were the most important determinants of the magnitude of this inorganic CO₂ flux. In the extreme cases of air-dried saline/alkaline soils, this inorganic process was predominant. While the diurnal flux measured was zero sum, leaching of the dissolved inorganic carbon in the soil solution could potentially effect net carbon ecosystem exchange. This finding implies that an inorganic module should be incorporated when dealing with the CO₂ flux of saline/alkaline land. Neglecting this inorganic flux may induce erroneous or misleading conclusions in interpreting CO₂ fluxes of these ecosystems.

Projections of climatic change and its relationship with carbon dioxide (CO₂) have attracted a great deal of scientific and public attention concerning carbon (C) cycling¹. As one of the major determinants of the C balance in terrestrial ecosystems², soil CO₂ flux, is considered an important regulator of climate change³. Conventionally, the soil CO₂ flux is interpreted in the context of an unstated hypothesis that biotic processes, including microbial oxidation of soil organic matter and litter fall and root respiration, largely determine the processes of CO₂ release from soil⁴. Not surprisingly, most research has centered on defining empirical relationships between soil CO₂ fluxes and specific climatic parameters, such as temperature^{5,6}, precipitation⁷ and soil water content – in order to create basic regressions to predict fluxes in changing environments^{5,7–9}.

However, in some arid and semi-arid systems, both positive and negative CO₂ fluxes (including negative fluxes at night), which could not be attributed to conventional biological processes, have been observed with both chambers and open- or close-path eddy systems^{10–12}. Possible explanations have been proposed to rationalize these ‘anomalous fluxes’. Growth of cryptobiotic crust organisms (lichens, mosses and cyanobacteria) were proposed to account for a significant portion of the C uptake in the Mojave Desert¹¹. Night time uptake of CO₂ by CAM plants is another biological explanation for low or negative night time flux rates¹³. Abiotic processes such as leaching^{14,15}, photo-degradation^{16–18} and CO₂ dissolution^{19,20}, can also contribute to CO₂ flux, which had been largely neglected in the global C cycle¹¹. Globally, soils contain huge amounts of inorganic C (750–950 Pg C)^{19,21} that could potentially be an active participant in short-term CO₂ fluxes, particularly in arid areas with large amounts of soil carbonate^{19,22}. Large daily CO₂ emissions in association with rainfall events during the dry season were proposed to result from equilibrium reactions occurring in carbonate soils^{19,22}. More importantly, carbonate or soil CO₂ dissolution could cause CO₂ flow into soil (i.e. negative flux) on short time scales (hourly). Such negative fluxes have been reported under certain conditions, such as in a dry valley²³ and hot desert soils^{12,13}, and might temporally dominate the soil CO₂ flux¹². For example, large CO₂ uptake was observed either *in situ* or after sterilization in the Gubantonggut Desert, western China, and was attributed to absorption by saline/alkaline soil¹². This provoked a debate on deserts as the location of the long-sought ‘missing sink’ for C^{10,24}. Namely, there is strong evidence suggesting that inorganic processes can contribute significantly to the total soil CO₂ flux²⁰. However, the mechanisms and magnitude of such fluxes are still a matter of controversy^{10,24}.

Using data from a field, laboratory and modeling study, we propose that the flux measured after sterilization of a saline/alkaline soil was predominately the effusion-dissolution of CO₂ entering the soil solution during the night



or leaving the soil solution during the day (hereafter: ‘inorganic flux’). We show that this inorganic process can contribute significantly to the total soil CO₂ flux for saline/alkaline soils and dominates the soil CO₂ flux when soils are dry, with carbonate in the soil not significantly involved. After experimentally partitioning the total soil CO₂ flux into organic (conventional soil CO₂ flux) and inorganic fluxes, a process-based soil CO₂ equilibrium-transport model was built to quantify this inorganic flux. This model could easily be incorporated into C flux models for soils of differing degrees of salinity/alkalinity. Neglecting this inorganic flux could induce erroneous or misleading interpretations of the C fluxes of arid and semi-arid ecosystems that make up nearly half the land surface^{24,25}.

Results

Field measurement of under-canopy and inter-plant CO₂ fluxes.

Soil CO₂ fluxes under the canopy were significantly higher than those in inter-plant spaces (Fig. 1), with rates ranging from -0.28 to 1.76 and -0.42 to 1.24 $\mu\text{mol m}^{-2}\text{s}^{-1}$ for under the canopy and inter-plant spaces, respectively. Both under the canopy and in inter-plant spaces, the soil CO₂ fluxes exhibited similar diurnal pattern over the growing season. Most noteworthy was that the soil CO₂ fluxes were always negative during night in inter-plant spaces over the whole growing season, which was unexpected according to the conventional definition of soil respiration. Any biological uptake of CO₂ (such as photosynthesis of CAM plants or cryptobiotic crusts) can be ruled out as we were measuring on bare soil.

Laboratory verification of the diurnal flux. To rule out the possibility of instrumental error and be sure the negative flux was real, we checked the instrument and measuring procedure carefully by using inert quartz sand as the soil matrix to verify the flux. When pure dry quartz sand was used as a replacement for soil, the fluxes were always close to zero (Fig. 2); when distilled water was added into quartz sand,

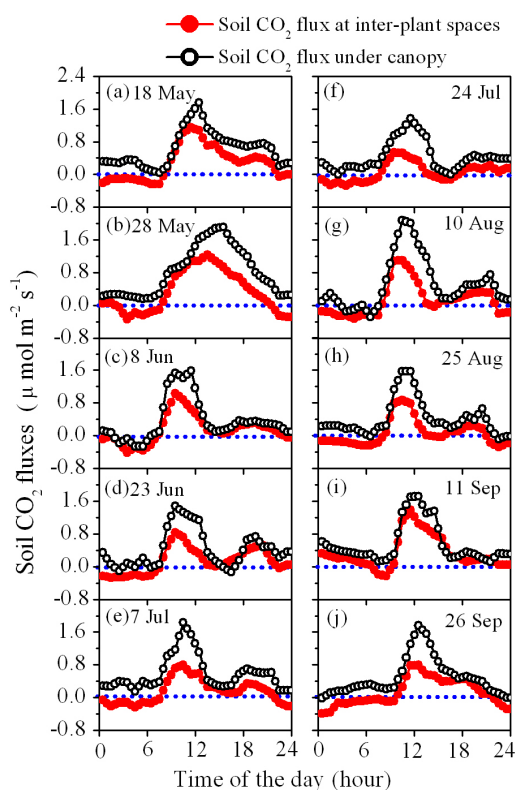


Figure 1 | The diurnal courses of soil CO₂ flux under the canopy (hollow circles) and in inter-plant spaces (solid circles) over 10 clear sampling dates in 2009.

there were small fluxes in a range of ± 0.1 $\mu\text{mol m}^{-2}\text{s}^{-1}$. In contrast, flux rates of approximately ± 1 $\mu\text{mol m}^{-2}\text{s}^{-1}$ were observed when sterilized soil solution (pH = 8.97, EC = 6 dS m⁻¹) was added to the quartz sand. Hence, the lack of detectable variations of flux for the quartz sand alone indicated that the instrument was reliable. The strong diurnal pattern of the flux that related to saline soil solution was not an artifact – a process other than oxidation of organic carbon (either biotic or abiotic) must have occurred in soil, which should be the cause of the negative flux (Fig. 1).

Partitioning the total soil CO₂ flux into organic and inorganic components.

To partition the total soil CO₂ flux into inorganic ($R_{\text{inorganic}}$) and organic (R_{organic}) fluxes, we measured the fluxes of sterilized and unsterilized soils with 10% water content synchronously. The sterilized and unsterilized soils were considered inorganic and total fluxes respectively, with the difference between the two representing the organic CO₂ flux, which exhibited a single peak and was in the range of 0.08 – 0.93 $\mu\text{mol m}^{-2}\text{s}^{-1}$ (Fig. 3). We use the term “inorganic” flux to differentiate between abiotic flux (which could include abiotic C oxidation processes) and the effusion/dissolution process for reasons that will become apparent during the results and discussion sections.

Total soil CO₂ flux was positive in the daytime and peaked during 12:00–16:00. More important, the total soil CO₂ flux could be negative under the influence of the inorganic flux (Fig. 3d and e), which had parallel diurnal patterns of a single peak at 12:00–14:00 similar to organic flux and varied in a diurnal sinusoidal waveform. Diurnal variations of $R_{\text{inorganic}}$, R_{organic} and R_{total} were all highly associated with variations in soil temperature (r^2 values were within 0.49–0.87 for all measurements, $n = 48$, $P < 0.01$). In addition, the amplitude of the inorganic flux increased with increased pH, which climbed from 0.14 at pH 7.19 to 0.65 at pH 8.55. To evaluate the contribution of the inorganic flux to total soil CO₂ flux, mean instantaneous (e.g. hourly) ratios were calculated for the five different soils when the inorganic flux was positive, which ranged within 0.14–0.39 in a positive relationship with pH ($r^2 = 0.89$, $P < 0.01$) (Fig. 3f). By contrast, there was no significant difference between the total soil CO₂ flux and the inorganic flux for the air-dried soils (Fig. 4) – when the soil was sufficiently dry, total soil CO₂ flux all came from the inorganic flux. Regardless of being dry or wet, the inorganic flux was driven by soil temperature on a daily scale and its magnitude was mainly determined by soil pH (Figs. 3 and 4).

Model validation. In general, the inorganic CO₂ flux was negative (i.e. into the soil) at night and positive (or outward from soil to atmosphere) during the day, with greater diurnal amplitude for soils with high EC and pH (Fig. 5). The amplitude of the inorganic flux varied from about 0.10 $\mu\text{mol m}^{-2}\text{s}^{-1}$ for EC = 5 dS m⁻¹ and pH

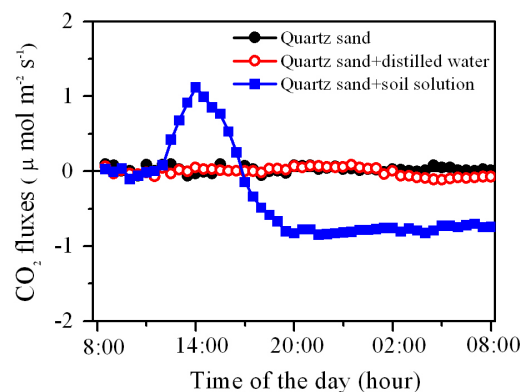


Figure 2 | Verification of the measuring reliability using different matrices (quartz sand only, quartz sand with distilled water and quartz sand with sterilized soil solution).

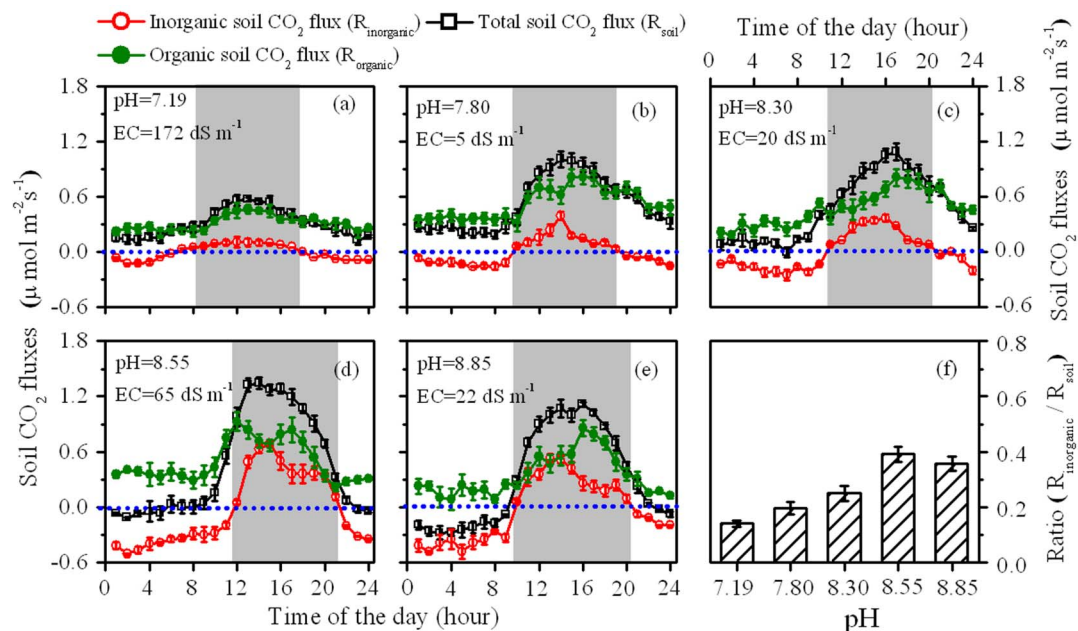


Figure 3 | The contribution of inorganic CO₂ flux to total soil CO₂ flux in soils varying in pH and EC at soil moisture content of 10% and the overall contribution of inorganic flux at different pHs [pHs for (a)–(e) were 7.19, 7.80, 8.30, 8.55 and 8.85, respectively]. The shaded parts indicate the period in which the inorganic CO₂ fluxes are positive and the instantaneous ratio of inorganic CO₂ flux to total CO₂ flux were calculated (f). Error bars represent standard error of the mean.

7.80, to as high as 0.51 μmol m⁻² s⁻¹ for EC = 126 dS m⁻¹ and pH 8.30. There was good agreement between measured and simulated inorganic fluxes both in the magnitude and diurnal pattern (Fig. 5). Linear regressions between simulated and measured inorganic fluxes yielded regression coefficients close to one (Supplementary Fig. S1).

The inorganic CO₂ flux was positive during the day and negative at night with a zero sum over 24 h (Figs. 3–5). To quantify the inward and outward amounts of CO₂, exchange rates were modeled for a range of pH and EC with 10% water content (Fig. 6). The amount of CO₂ exchange was in the range of 35.0–1749.4 mg CO₂ m⁻² d⁻¹ for the given range of pH and EC (Fig. 6).

Sensitivity analysis of the model. Table 1 presents the sensitivity of the magnitude of inorganic CO₂ exchange to an increase of 5% in the model parameters over a day. Each change in an input parameter of the model was simulated under real environmental conditions. The parameters were listed in order of importance of their impact on the inorganic processes (Table 1) – pH was the dominant parameter for inorganic processes, with a more significant impact than others parameters: a 5% increase in pH produced an increase of 138% inorganic CO₂ exchange. This is easily explained by an exponential increase in solubility of CO₂ in soil solution with a pH increase²⁶.

Discussion

The integration of these results provides new insight into the ‘anomalous’ negative fluxes observed in saline/alkaline soils. Thus, when slow changes in soil organic or inorganic C storage, pools of C in biological soil crusts or CAM plants cannot explain the observed large net uptake^{10,13,24}, the observations are not necessarily wrong^{10,24,27,28}. An inorganic process – the effusion and dissolution of CO₂ into and out of the soil solution (Figs. 3–5) – can make the nighttime soil CO₂ flux negative, and accounts for the ‘anomalous’ flux.

The inorganic flux, driven by diurnal temperature variation, was derived from the change in the size of the reservoir of dissolved inorganic carbon (DIC) in the soil solution as determined by Henry’s Law^{29–31}. The size of this reservoir increases during the day as temperature increases, and decreases at night as temperature decreases (Figs. 3–5).

For the positive CO₂ fluxes, it may be argued that these fluxes could derive from other abiotic oxidation processes, such as thermal degradation and photo-degradation^{16–18}. While we can not rule out a contribution from abiotic oxidation processes to the positive CO₂ flux occurring during the day, the organic matter content in saline/alkaline soils of the arid zone is very low^{6,7,32}. More important, these

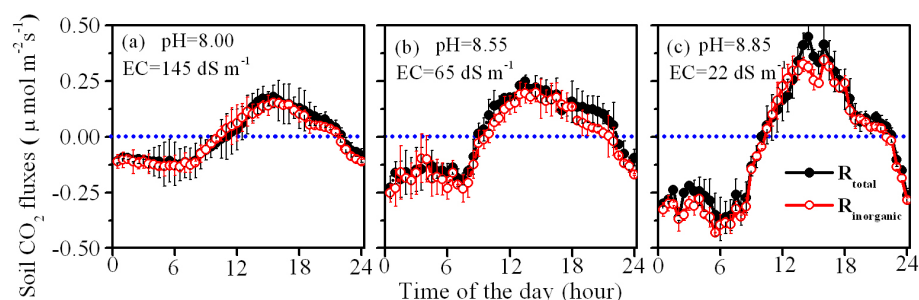


Figure 4 | The contribution of inorganic CO₂ flux to total soil CO₂ flux in soils varying in pH and EC in air-dried condition. Error bars represent standard error of the mean.

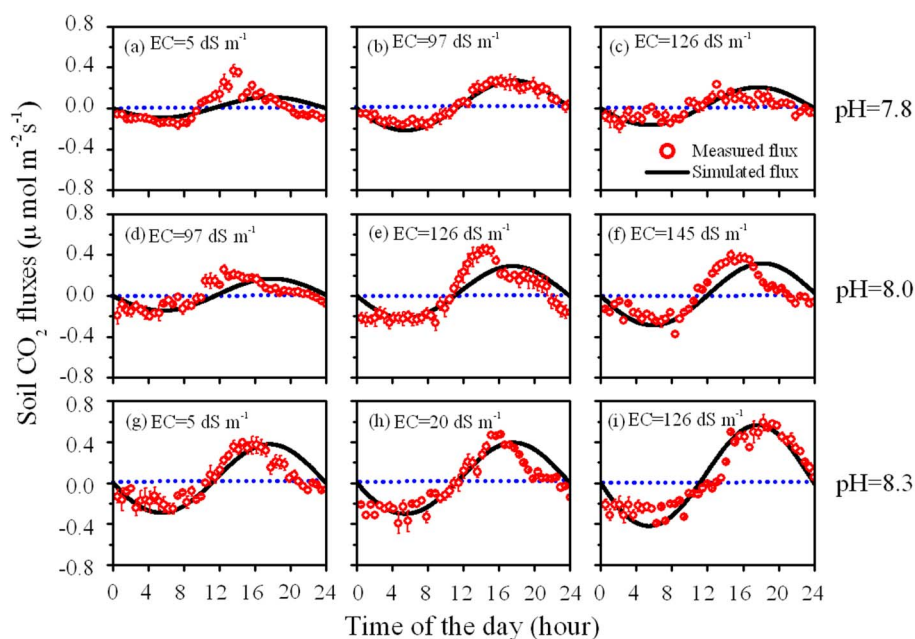


Figure 5 | Diurnal patterns for simulated (solid lines) and directly measured (hollow circles) inorganic soil CO_2 flux in soils with different pH and soil salt content (EC) at soil moisture content of 10%. (a–c) pH 7.80; (d–f) pH 8.00; and (g–i) pH = 8.30.

other abiotic processes can not explain the negative CO_2 fluxes occurring at night, and the modeling suggests that CO_2 effusion/dissolution adequately explains the magnitude of both the positive and negative fluxes observed in the field and laboratory experiments (Figs. 3–5). In addition, the zero sum total flux (Figs. 3–5) would also suggest that other biotic and abiotic processes are not a significant source of positive C flux in these soils. Therefore, within the context of the current study, we assume the measured CO_2 fluxes from the sterilized soil are predominantly derived from the inorganic effusion/dissolution of CO_2 into and out of the soil. In acid soils and/or soils rich in organic matter, the effusion/dissolution process would likely be insignificant in comparison with biotic (or other abiotic sources of) soil C flux, but the nature of the fluxes can still be easily distinguished by the diurnal pattern.

Although the diurnal inorganic effusion/dissolution process was zero sum (Figs. 3–5), the DIC itself could still be a significant C reservoir in saline/alkaline soils²⁹, mainly determined by pH and soil moisture (Fig. 6, Table. 1). According to the simulation, the amount of DIC contained in the $100 \text{ cm} \times 100 \text{ cm} \times 40 \text{ cm}$ soil pillars in the present experiment was in the range of 0.178–0.183 mol under normal saline conditions (for parameters listed in Table 1), which is similar to the C contained in up to 11 m^3 of air with CO_2 concentration of 380 ppm. Assuming a soil moisture content of similar value, DIC in the soil could be considerably greater in the field, as soil CO_2 partial pressures ($p\text{CO}_2$) are 10–100 times higher than those of the atmosphere³³. In the absence of carbonate, dissolution from soil $p\text{CO}_2$ would account for all C present in DIC³⁴. Thus, this inorganic flux can occur with or without carbonate in the soil, provided

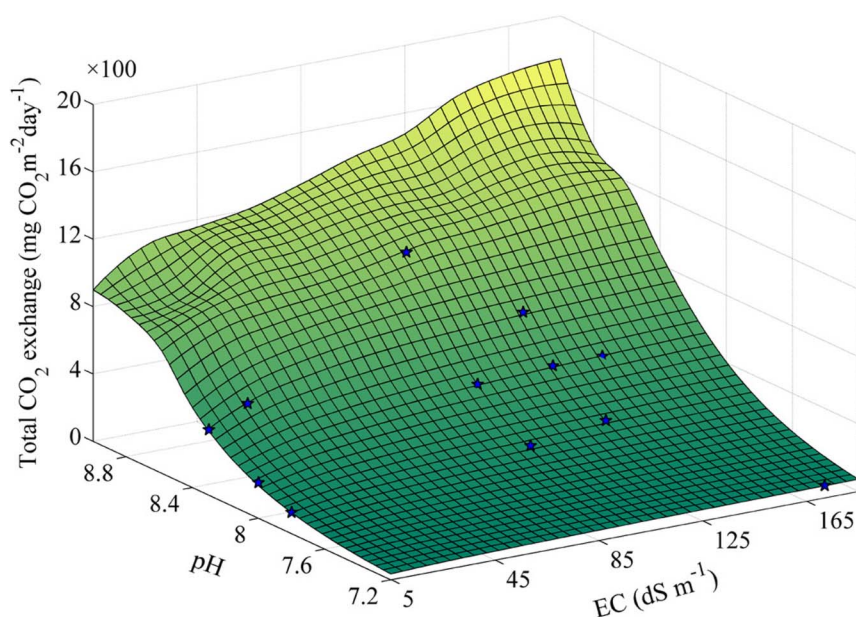


Figure 6 | The modeling output of daily inorganic CO_2 exchange for soils with different pH and EC at soil moisture content of 10%. The black stars indicate the inorganic processes that were validated by directly measured data.

Table 1 | Sensitivity of the magnitude of inorganic CO₂ exchange to the variation in model parameters

Parameters, α	Parameter nominal value	Δ (total CO ₂ exchange)(%), induced by $\delta\alpha = 5\% \alpha$
pH	8.25	1.3785
CO ₂ partial pressure (CO ₂ concentration), P_{CO_2}	0.0005 atm	0.0500
Soil moisture content, V_{water}	10%	0.0500
CO ₂ diffusion coefficient in the atmosphere, D_{g0}^a	$1.39 \times 10^{-5} \text{ m}^2\text{s}^{-1}$	0.0405
Electrical conductivity, EC	95 dS m ⁻¹	0.0107
The average temperature at 5 cm in June, T_5	33.95°C	0.0060
Universal gas constant, R	8.31451 J mol ⁻¹ K ⁻¹	0.0000
The average amplitude of temperature at 5 cm in June, A_{5n}	12.85°C	0.0000
Soil bulk density, d	1.25 g cm ⁻³	0.0000

the soils are alkaline. Dissolution or precipitation of carbonates implies CO₂ consumption or emission^{20,35}, which affects the concentration of DIC and total alkalinity (A_T)³¹, but the direct contribution to DIC has been shown to be relatively small³¹. Karberg *et al.*³¹ used an isotopic mixing model to partition the source of DIC and revealed that approximately 90% of DIC-C was from soil pCO_2 rather than carbonate salts. Other salts (whether carbonate or non-carbonate) play a similar role in changing the ionic strength and A_T of the soil solution, and therefore also affect the DIC content in the soil solution²⁰.

We suggest there could also be a seasonal inorganic flux variation from winter to summer, as soil temperature varies as it does on a daily scale (Figs. 3–5). Rainfall or irrigation processes that change the soil moisture would also certainly alter this inorganic CO₂ flux, as it not only changes the porosity occupied by soil air or soil solution, but also changes the EC or A_T of the soil solution. Although in our experiment inorganic flux on a diurnal basis resulted in no net gain or loss of C, DIC could be lost from the soil by leaching, runoff or fluctuations in groundwater. Losses of DIC through such process would be an additional source of C in Net Ecosystem Exchange (NEE)^{1,14,15}.

We refrain from going into further detail concerning the effect of soil moisture because of its complex and multiple impacts on this inorganic process. However, our data indicate that the drier the saline/alkaline soils are, the more predominant the inorganic process will be in determining the soil CO₂ flux (Figs. 3 and 4). If this inorganic C flux is significant for the approximately one-fourth of the global land that comprises arid saline/alkaline soils, why has such a significant flux been neglected for so long? In most ecosystems, the soil CO₂ flux is positive during both day and night, and the negative flux resulting from this inorganic process is hidden by a measurable positive CO₂ flux at night. Under certain extreme conditions, such as saline deserts¹² or Antarctic soils³⁶, where flux rates are inherently low due to low biotic activity, the inorganic flux is more pronounced and is then comparable to and even exceeds the magnitude of the organic flux, resulting in a negative CO₂ flux at night (Fig. 1). The relative contribution of inorganic flux to total CO₂ flux ($R_{inorganic}/R_{total}$) is the key to discerning where this inorganic process will be important. When the transient rate of the inorganic flux is lower than the organic flux, as in most ecosystems, the measured soil CO₂ fluxes are still positive but could potentially be underestimated at night.

The underestimation of night time flux rates could have further implications for calculations of ecosystem respiration because it is the regression between respiration and temperature at night that is used to extrapolated ecosystem respiration during the daytime^{6,37,38}. In ecosystems with saline/alkaline soils, underestimation of night time flux would significantly underestimate the daytime C efflux and thus result in an overestimation of the net primary productivity.

In summary, the recognition of an inorganic component in the soil C flux has widespread consequences for the study of the global C cycle. We suggest an inorganic module, such as the model presented in the current study, should be added for the saline/alkaline half of

the global land. Otherwise, C cycling analysis could be inaccurate in both mechanism and quantification.

Methods

Site description. Field soil CO₂ flux measurements were conducted at the Fukang Station of Desert Ecology (44°17'N, 87°56'E and 475 m a.s.l.), Chinese Academy of Sciences. The climate of the region is arid temperate with annual mean temperature of 5–7°C and mean annual precipitation of 160 mm. The main soil types were classified as Solonchaks in the FAO/UNESCO soil classification system¹². The soil is silty clay-loam with high salinity/alkalinity [electrical conductivity (EC) > 4 dS m⁻¹, pH > 8.2 for soil solution of soil/water ratio of 1 : 5], with the soil solution mainly consisting of sulfate and chloride salts. Total nitrogen and organic C contents of the soil are 0.068 and 1.064%, respectively⁷. The plant community is dominated by *Tamarix* spp., a deep-rooted halophyte shrub³⁹, with canopy coverage of approximately 17% of the land surface.

In situ measurement of soil CO₂ flux. Soil CO₂ flux was measured during the growing season (from May 5 to Oct 10) in 2009, with an LI–8150 Automated Soil CO₂ Flux System, equipped with six long-term monitoring chambers. Soil collars were arranged along a projecting line from the center of a shrub with average crown diameter to interplant space; distances to the center were 0.5, 1, 2, 3, 4 and 5 m, respectively. More details about field measurement can be found in Ma *et al.*⁷ In this study, we only compared soil CO₂ flux under the canopy with that in inter-plant spaces (distance to center is 5 m) to capture spatial variation derived from the effect of the plant canopy⁴⁰.

Control experiment. To determine the potential contribution of inorganic flux to total soil CO₂ flux, we compared the fluxes between sterilized and unsterilized soils. An autoclaving method was found to be most suitable³⁵ and was used in this study. In total, 14 types of soil samples were collected from different places to represent pH and EC gradients in nature. Soil samples were ground, air-dried, and sieved (16-mesh) to remove gravel and roots. The samples were then well mixed to make them homogeneous. Soil pH and soil EC were determined by a Sartorius PP–20 Professional Meter (Sartorius, Germany) with soil solution centrifuged from water-saturated soil.

Controlled experiments were carried out on air-dried soils (with residue moisture at approximately 2.5%) and soils with moisture content of 10% (v/v). These levels of soil moistures were chosen because soils in arid zone are generally dry due to high evaporation and low precipitation. For the 10% treatment, distilled water was first added to both unsterilized and sterilized soils to attain a 10% moisture level. Then soils were put into six metal drums (three for sterilization and another three for natural conditions), whose bottom were sealed. The heights of the drums were 40 cm, because the diurnal variation of soil temperature below 40 cm was < 1.5°C in the field and was assumed to be negligible in the current study. For sterilized soils, the tops of the metal drums were sealed by layers of filter and brown paper to minimize water infiltrating into the soil, and were sterilized in a medical autoclave for 24 h at 120°C. After sterilization, soil drums were placed in a UV-sterilized room to allow soil cores to equilibrate with the surrounding conditions. To increase the comparability of the results between sterilized and unsterilized soil, the drums filled with control (i.e. unsterilized) soils were also covered with filter papers at the top and balanced with their surroundings synchronously. The metal drums were then reburied in the field to maintain natural fluctuations of soil temperature. The soil surface in the drums was as at an equivalent height to the surrounding soil. CO₂ flux was measured every 30 min for 2 d for each set of soil samples. For the air-dried soil, the soil was put into drums directly, and sterilization and measurements processes were same as the soils with 10% moisture.

To confirm the accuracy of the LI–COR 8150 measurements, we compared the surface CO₂ flux from artificial matrices, with three different treatments: quartz sand, quartz sand with distilled water and quartz sand with sterilized soil solution. The purpose of using analytically pure quartz sand was to check whether the instruments would measure zero flux when it was expected to be zero. By contrast, the difference between treatments of quartz with soil solution and quartz sand with distilled water was to determine whether “anomalous fluxes” occurred under these controlled and sterilized conditions. Before measurements, distilled water and sterile soil solution



were added to corresponding drums to attain a 10% moisture level and reburied in the field after equilibrium. Measurement processes were the same as that of soil CO₂ flux.

Soil temperature was measured at 5, 10, 15, and 20 cm below the soil surface in a soil profile close to the chambers, using a thermocouple connected to LI-8150 long-term chambers. The soil moisture content was determined by conventional oven-drying method after each set of measurement.

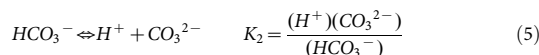
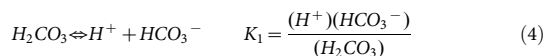
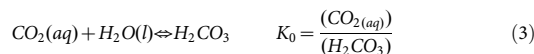
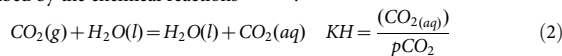
Model description. CO₂ flux in or out of the soil surface is considered to be the combined result of two major processes: the production or absorption of CO₂ and gas transport process^{41,42}. Based on the one-dimensional (vertical) soil CO₂ transport model described by Nickerson & Risk⁴³ and Phillips *et al.*⁵, we add a new function of CO₂ concentration change adjusted by effusion or dissolution equilibrium between CO₂ and soil solution^{26,29,30,44}, which was regulated by temperature. The vertical CO₂ flux can be expressed by the following mass balance equation^{41,42}:

$$\frac{\partial C_t}{\partial t} = -\frac{\partial}{\partial z}(F_{diff} + F_{adv}) + P_{Rs} \quad (1)$$

F_{diff} and F_{adv} describe the CO₂ fluxes caused by diffusion in the gas phase and by advection of soil air, respectively; P_{Rs} represents the total CO₂ production by the respiration source, and in our study $P_{Rs} = 0$ for we assume all the biological processes or microorganism's activities were excluded by the pretreatments of root removal and sterilization; t denotes time (s) and z the depth below the soil surface.

The modeled environment assumes a well-mixed atmospheric boundary layer (Supplementary Fig. S2). To simplify the model, the total soil column was considered homogenous, and total soil porosity (Φ) was considered to be constant with depth and any air/water-filled pore space during the simulation keep constant over the length of the entire soil column. As changes in soil water volume are always matched by changes in gas volume in the opposite direction.

Submodel of the effusion-dissolution equilibrium of CO₂ with soil solution. In the absence of biotic processes, the chemical equilibria in the soil-water-air continuum can be described by the chemical reactions^{26,29,30,44}.



where pCO_2 is the partial pressure of CO₂ in the soil air (atm); KH is Henry's Law constant; and K_0 , K_1 and K_2 are equilibrium constants of dissolution, and first and second order dissociation reaction constants for carbonic acid, respectively (temperature dependence of the constants for saline and alkaline soils are listed in Supplementary Table S1). So, the total amount of DIC was calculated as the sum of all carbonaceous species resulting from CO₂ dissolution³¹, which can be obtained from equations (2)–(5).

Submodel of CO₂ transport component. Under the assumption of horizontal homogeneity, where the horizontal loss or gain of CO₂ and the dispersion of CO₂ in the gas phase caused by vertical gas movement are negligible, one-dimensional CO₂ transport in each layer of soils exchanges gases along soil CO₂ concentration gradients with its nearest two neighboring soil layers, governed by Fick's First Law^{5,41,42}:

$$F_{diff} = -D_g^* \times \frac{\partial Cg}{\partial z} = -\xi_g \times D_g^* \times \frac{\partial Cg}{\partial z} \quad (6)$$

where ∂Cg is the difference of CO₂ concentration between two neighboring layers; D_g^* and D_g^* are the effective diffusion coefficient of CO₂ in the atmosphere and soil respectively; and ξ_g is the tortuosity factor of gas diffusion through the soil as a function of air-filled porosity^{45–48}.

Up to now there has been no effective method to quantify the tortuosity factor of CO₂ diffusion in the liquid phase. However, the diffusion of CO₂ in the liquid phase is about 10000 times lower than that in the gas phase, thus the contribution of the liquid phase to the total effective diffusion is far less than that of gas phase diffusion, except when soil is close to saturation⁴¹. So ignoring liquid phase diffusion will not cause a serious error in the modeling, and the new CO₂ concentration in each layer at each model time-step (e.g. 1 s) was calculated as^{43,49}:

$$C(z, t+1) = C(z, t) + \frac{F_{diff}(z+1, t+1) - F_{diff}(z, t+1) + CO_2 change(z, t+1)}{V_{air} \cdot L/N} \quad (7)$$

where $F_{diff}(z+1, t+1)$ is the CO₂ flux from the layer (z) below, $F_{diff}(z, t+1)$ is the CO₂ flux leaving the layer z ; L is the total depth of the soil column and N is the total number of soil layers. $CO_2 change(z, t+1)$ is the change of CO₂ concentration at layer z at time ($t+1$), which can be expressed by:

$$CO_2 change(z, t+1) = [DIC(z, t+1) - DIC(z, t)] \times Vwater \quad (8)$$

For the numerical solution of equation (1), the soil was divided into 40 horizontal layers with thickness of 1 cm. Soils in metal drums were assumed to exhibit no

respiratory CO₂ production after sterilization treatment. Soil porosity, pH and CO₂ concentration for each soil were set constant with time and soil depth. The model was programmed and run in Matlab 7.7. To minimize model run time, the model was initialized for a steady state and the initial CO₂ concentration in the atmospheric layer and at each soil depth was typically assigned to a constant CO₂ concentration, 380 ppm. The time steps used in the iterative solving of the model equations was 1 s and model output to file was 1 min.

Simulated inorganic fluxes from the soil surface were validated by the half-hourly flux data measured after soil sterilization treatment with soil moisture content of 10%.

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Author contributions

All authors commented on manuscript at all stages. Y.L. developed the concept of the paper and oversaw the study; J.M., W.Z.Y. and Z.X.J. did the *in situ* measurements of soil CO_2 flux and the sterilization experiment; J.M. and Y.L. analyzed all the data and wrote the paper; B.A.S worked on every version of the paper and had significant contribution in structuring and presenting the paper.

Additional information

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