The effect of water repellency on the short-term release of CO_2 upon soil wetting

Abstract

The spike in carbon dioxide (CO_2) observed after rewetting of dry soils, known as the 'Birch effect', can contribute substantially to total soil carbon (C) emissions, however, the exact mechanisms and timings underlying this sudden CO_2 release remain unclear. The amount of applied water and duration of the previous dry period are considered the main factors affecting the magnitude of the CO_2 peak, but the preceding change in soil wettability, triggered by low soil water content, could also be an important contributor.

We investigated the effect of soil water repellency (SWR, assessed by water drop penetration time test) on the short-term release of CO_2 upon wetting of dry soils with different water quantities. The experiments were conducted under laboratory conditions using homogeneous and autoclaved soil from two locations in South Wales (UK) in both wettable and extremely water-repellent states. The CO_2 efflux was measured using chambers above and below the samples. Upon wetting, CO_2 efflux was up to 10 times lower in water-repellent soils as a result of rapid percolation through preferential pathways, with only a small amount of water (up to 10%) retained in the soil. Total CO_2 efflux was proportional to the water retained in the soil after infiltration, suggesting that the release of CO_2 occurred only from limited pore-spaces of the soil. The quick CO_2 release suggests that chemical or biochemical processes, rather than microbial respiration, is the main source of CO_2 efflux in this study. Part of the CO_2 released was transported to the bottom chamber, which under natural conditions could enhance the entrapment of gas in the subsoil. This study shows that alterations in the water-filled pore-space as a result of SWR significantly reduced the CO_2 efflux upon wetting and suggests that SWR could be a key factor when investigating and predicting C fluxes.

Keywords: hydrophobicity, Birch effect, CO_2 pulse, C emissions, soil degassing, rain pulses

Highlights

- Low CO_2 pulse in water-repellent soils compared to high pulse in wettable soils.
- Less than 10% of total water applied retained in water-repellent soils.
- Total flux was controlled by the amount of water retained in the soil after wetting.
- Flux transported downwards might contribute to air entrapment deeper in the soil.

1. Introduction

Rewetting of dry soils is associated with a large pulse of carbon dioxide (CO_2) commonly known as the 'Birch effect' (Birch, 1958). The overall contribution of these short-lived but high magnitude spikes of CO_2 to the total soil carbon (C) flux could be large (Leon et al., 2014; Smith et al., 2017), especially with increased frequency and duration of dry spells, which are becoming more common with the climatic change (Coumou and Rahmstorf, 2012; Trenberth et al., 2013). Although the 'Birch effect' has been studied for over 50 years, there is still a lack of consensus about the exact causes and factors affecting the size and duration of the CO_2 pulse (Fraser et al., 2016; Waring & Powers, 2016) which are still not included in the global terrestrial C emissions models (Moyano et al., 2013).

Many studies suggest that the 'Birch effect' originates mainly from a quick restoration of microbial respiration, which is very low in dry soils due to restricted water availability for microorganisms and the disconnection of soil pores (Borken and Matzner, 2009). After rainfall, the sudden input of water reconnects the pore system and mobilizes previously unavailable C (Kim et al., 2012; Schimel, 2018) resulting in a boost of microbial activity and a spike in soil CO_2 efflux. The size of the CO_2 pulse is expected to increase with the amount of water added (Lado-Monserrat et al., 2014; Muhr and Borken, 2009; Sponseller, 2007). Although the boost in microbial respiration is probably the largest contributor of CO_2 to the 'Birch effect', some studies argue that the lag period between the wetting and the reactivation of microbial activity can last several hours (Meisner et al., 2017). It has, therefore, been suggested that the degassing of soil might be the main contributor of the CO_2 pulse during the early post-wetting phase (Kim et al., 2012; Norman et al., 1992). Soil gas is not always emitted immediately. Degassing of CO_2 stored in the pore-space can make up a substantial fraction of the total CO_2 response to wetting during extreme rainfall events (Maier et al., 2010; 2011; Huxman et al., 2004; Inglima et al., 2009; Liu et al., 2002).

'Birch effect' studies have focussed mainly on the duration and intensity of the drought (de Nijs, 2018; Göransson et al., 2013; Meisner et al., 2015), precipitation rates (Lado-Monserrat et al., 2014; Muhr et al., 2008) or the type of wetting (Smith et al., 2017) as the main factors affecting the size of the pulse. In a recent study (Sánchez-García et al., 2020) we have shown that restricted infiltration, caused by soil water repellency (SWR), can also alter the CO_2 efflux response to wetting substantially. SWR is a transient property of many soils, especially those under permanent (Doerr et al., 2000) and stress-tolerant vegetation at low soil water content (SWC) (Seaton et al., 2019). SWR is primarily caused by the coating of soil particles by hydrophobic organic compounds and can become especially severe after dry periods or fires (DeBano, 2000; Doerr & Thomas, 2000). Current changing climate conditions resulting in higher incidence and intensity of droughts will likely enhance the occurrence and severity of SWR (Goebel et al., 2011). By inducing changes in soil microbial properties and community structure in response to environmental stressors like drought, soils with stress-tolerant vegetation can develop hydrophobic layers in order to adapt to low water availability (Seaton et al., 2019). Thus many soils subjected to dry spells change their hydrological properties by developing this lack of wettability. Robinson et al. (2019) highlighted the need to incorporate the dynamics of hydraulic properties in response to such biological feedbacks.

Water-repellent soils do not allow free infiltration of water; instead, water either runs off the terrain's surface (Doerr et al., 2003) or beads up and percolates quickly into the subsoil through preferential flow paths, leaving much of the topsoil dry (Doerr et al., 2000; Ritsema and Dekker, 1994). The infiltration patterns of water-repellent soils are thus substantially different to wettable ones, and therefore, the CO_2 efflux in response to wetting of such soils is unlikely to be the same.

Despite this, evidence of water repellency-induced changes in soil C dynamics remains sparse. A few studies have focused on respiration rates in water-repellent soils (Goebel et al., 2007; Lamparter et al., 2009) or the overall effects of SWR on CO_2 fluxes (Urbanek and Doerr, 2017) rather than on short-term spikes of CO_2 after rainfall events. In a previous study, (Sánchez-García et al., 2020) we presented evidence that SWR reduces the CO_2 pulse after wetting of soil; however, the effect of the rewetting rate on the magnitude and the duration of the CO_2 pulse in water-repellent soils have remained unclear.

In this study we address this research gap and aim to improve understanding of the effect of SWR on the CO_2 efflux upon rewetting. We hypothesise that i) the amount of released CO_2 is proportional to the rewetting rate of the soil and ii) the initial CO_2 pulse can be mainly caused by the physical release of gas present in soil pores by infiltrating water rather than a spike in microbial activity.

2. Research design and methods

This study involves a series of wetting experiments on homogenised soil under laboratory conditions. Soil material used for the experiments was autoclaved to remove the contribution from microbial respiration to CO_2 fluxes and to isolate the physical release of CO_2, but also to obtain soils with contrasting wettability that otherwise have similar physico-chemical properties (Urbanek et al., 2010). Autoclaving of dry or very wet soils keeps the soils wettable, while at intermediate water content prior to autoclaving the soil turns water-repellent. All soil samples were subjected to one single wetting treatment applied from above to simulate a rainfall event. CO_2 fluxes were monitored above and below the soil sample in order to capture CO_2 movement upwards and downwards.

2.1. Soil sampling and preparations

Soil was collected from two locations in the Gower peninsula in South Wales (UK): a sandy loam referred to as Cefn Bryn (CB) (51° 35'N, 4° 10'W) and a loamy sand referred to as Southgate (SG) (51° 33'N, 4° 5'W) (Table 1). Soils at both locations are under natural grasslands with occasional animal grazing. The selected soils were used in previous studies (Urbanek et al., 2010; Gazze et al., 2017) and were known to develop SWR under natural conditions. The use of two types of soil material of different texture and SOM content allowed us to examine to what degree similar behaviour is observed in water-repellent soils despite differences in their physico-chemical properties.

Soil material was collected from approximately the top 2 to 10 cm over an area of 2 m^2, after careful removal of the grass root layer, brought to the laboratory, and air-dried and sieved to 2 mm. In order to prepare soil material of the same physico-chemical properties, but contrasting wettability, soil was pre-treated using a technique developed by Urbanek et al. (2010), which involved autoclaving the soil material at different SWC to obtain wettable and water-repellent soil. In order to determine an optimal SWC that results in the most contrasting wettability, a small sample of each soil at air dry, 10, 15, 40 and 50% SWC (grav.) was autoclaved (121 °C for 1 h) followed by oven-drying at 25 °C for 24 h to achieve similar SWC across all the samples (see Table 2 for a full range of results). Soil wettability was measured before and after autoclaving using the water drop penetration time (WDPT) test by placing 5 drops of water on the smoothed surface of a sample and categorised into the following classes (Doerr, 1998): wettable (< 5 s), slightly repellent (5–60 s), moderately repellent (60–600 s), strongly repellent (600 –3600 s) and extremely repellent (> 3600 s). Based on these tests, SWC for autoclaving was chosen to be 15% for both CB and SG soils to obtain extreme SWR (thereafter called CB-WR and SG-WR), and for the wettable soil 40% and 50% SWC was used for CB and SG respectively (thereafter called CB-NWR and SG-NWR). Although WDPT does not detect small variations in subcritical water repellency (Urbanek et al., 2007; Goebel et al., 2012), in this case WDPT was suitable given the contrasting wettability between our samples.

Other basic soil properties of the two soil materials were determined using standard methods; pH using a pH electrode in 1:5 dilutions of distilled water and $CaCl_2$, soil organic matter (SOM) using the loss of ignition method (Nelson and Sommers, 1996), particle size distribution using the laser diffraction method (LS230 laser particle size analyser, Beckman Coulter, Brea, CA) and particle density (ρ) following the Gay-Lussac Specific-Gravity Bottles method (Wofford and Vidrio, 2015 adapted). SWC was determined gravimetrically by moisture loss (105 °C, 24 h).

2.2. Soil wetting and CO_2 efflux measurements

Dry sterile soil at respective wettability (wettable and water-repellent) was packed into cylinders (8 cm diameter, 5 cm height) at bulk densities representative of field conditions: 1.16 and 0.82 g cm^{-3} for CB and SG respectively. The repacked cylinders were rewetted from above using a custom-made rainfall simulator fitted between the soil sample collar and the CO_2 flux chamber (Fig. 1). The rainfall simulator comprised one spiral tube with uniformly distributed drips, to ensure spatially uniform wetting, suspended 1 cm above the soil surface and connected via a tube to a large syringe to supply water. All cylinders received one single and uniform wetting application with water at an intensity of 100 mm h^{-1} to simulate a heavy rainfall event. The applied water was equivalent to 25, 50, 75 and 100% of water-filled pore-space (WFPS). WFPS for each soil was calculated by dividing volumetric water content by pore-space (PS) and pore-space was obtained from bulk density (dB) as follows: $PS = (1 - dB\ d_p^{-1}) \times 100$; assuming a particle density (d_p) = 2.65 g cm^{-3} (Blake, 2008). After wetting, water retained in the soil sample was quantified via the weight difference in the soil before and after wetting.

Each cylinder was suspended on a set of collars allowing monitoring of CO_2 concentration in the chamber above and below the sample simultaneously during the wetting and collection of drained water in the container below (Fig. 1). CO_2 concentration was monitored via a 10 cm survey chamber connected to an infrared CO_2 gas analyser system (IRGA) from above (Li-8100A, Li-COR Inc., Lincoln, NE) and a plastic container of a similar headspace connected to a separate IRGA CO_2 analyser system below the sample referred to as 'bottom chamber' (Li-8100A, Li-COR Inc., Lincoln, NE). A fine mesh was placed under the cylinders to allow any drainage of water while holding the soil inside the cylinder. The entire system (chambers, rainfall simulator and soil sample) was sealed to avoid gas leakage. The chamber's inbuilt pressure vent maintained ambient pressure inside the chamber (Fig. 1). The total time of post-wetting CO_2 fluxes monitoring was 150 min, the gas chamber remained closed for 30 min and vented for 1 min prior to the next closure.

The CO_2 concentration data obtained was fitted to a single-term exponential model, excluding the first 30 s of measurements, which is the typical time required to achieve steady mixing inside the chamber (LICOR, 2010). The following equation (Eq. 1) was applied to calculate CO_2 flux as the rate of change in CO_2 concentration released from soil (LICOR, 2010):

Eq. 1

$$Fc = \frac{10VPo}{RS(To+273.15)} * \frac{dC'}{dT}$$

Fc = soil CO_2 efflux (µmol m^{-2} s^{-1}), V = volume (cm^3), Po = initial pressure (kPa), S = soil surface area (cm^2), To = initial air temperature (°C) and dC'/dT = initial rate of change in water-corrected CO_2 mole fraction (µmol mol^{-1}). The CO_2 flux data below $R^2 \geq 0.95$ was rejected with a total of 10 and 15% of total rejected measurements above and below the sample respectively. The CO_2 flux graphs were created by calculating the mean flux (n = 3) for each treatment at each measurement time along with 95% confidence intervals. The Mann-Whitney U-Test was applied to test for statistical differences (accepted at $p < 0.05$) between wettable and water-repellent soils.

3. Results

3.1. CO_2 efflux before and after wetting

The CO_2 efflux from dry soils prior to wetting was very low. In all soils, the efflux measured in the top chamber was below 1 µmol m^{-2} s^{-1} and negligible in the bottom chamber (Fig. 2 and 3). The CO_2 efflux increased immediately in response to the wetting, which began exactly 20 min after the initial start of the observation. A clear increase in CO_2 efflux occurred in all wettable soils, with the maximum value observed during the wetting period for most samples, or immediately after the wetting period for SG-NWR with 25 and 50% rewetting rates. Fluxes in the wettable soils peaked 1 and 5 min after the start of wetting for CB and SG respectively. Under wettable conditions, large differences in the size of the pulse were observed between CB and SG soils with similar amounts of water added. In the CB-NWR soil the efflux peaks ranged between 5–7 µmol m^{-2} s^{-1}; whereas for SG-NWR soil, peak values were lower, ranging between 2.5–3.5 µmol m^{-2} s^{-1}. The larger amount of water added to the soil resulted in a longer duration of the peak, but did not affect the peak size. Overall, the size of the peak was higher but consistently shorter in CB soil, lasting between 11 and 20 min depending on the rewetting rate. For instance, doubling the rewetting rate from 25 to 50% increased the duration of the pulse by 4 min in both CB and SG soils, but no differences in the duration of the pulse were observed in SG soils with rewetting rates above 50%. In CB soils, the duration of the pulse increased by 4 min with a 75% rewetting rate but remained similar with a 100% rewetting rate.

The differences in the CO_2 efflux between wettable and water-repellent soils were very distinct. In both CB-WR and SG-WR, the size of the CO_2 pulse in the top chamber was up to ten times lower than in the corresponding wettable soils ($p < 0.001$ for both CB and SG soils). Peak sizes in water-repellent soils ranged from 1 to 3 µmol m^{-2} s^{-1} in the CB-WR, but in the SG-WR the CO_2 efflux hardly changed as a result of wetting (peak size 0.3 to 0.6 µmol m^{-2} s^{-1}). During the wetting of CB-WR, a distinct double peak was observed with rewetting rates above 50%. By the end of the observation period, at

145 min after the start of wetting, the CO_2 fluxes returned to pre-wetting values and no significant differences were observed between soils of contrasting wettability ($p = 0.229$).

Prior to wetting, the CO_2 flux in the bottom chamber, which represented the amount of CO_2 diffused downwards the soil profile, was low in both wettable and water-repellent soils. In CB-WR, CO_2 fluxes did not increase with the start of the wetting in the bottom chamber; instead, a pulse was observed towards the end of the wetting period. Similar to the top chamber, no CO_2 flux response was observed in SG-WR; whereas, in the SG-NWR soil, CO_2 fluxes increased with the beginning of wetting and a significantly higher pulse than in the water-repellent soil was observed ($p < 0.001$). No significant differences were observed between the pulses in the top and bottom chambers in both CB-WR and SG-WR ($p = 0.525$ and $p = 0.184$ respectively); however, the CO_2 pulses were higher in the top than in the bottom chamber for both CB-NWR and SG-NWR ($p = 0.001$ and $p < 0.001$ respectively).

3.2. Cumulative CO_2 efflux

The cumulative CO_2 efflux, calculated as the total CO_2 flux from both the top and bottom chambers combined, increased with the rewetting rate in wettable soils. The more water that was added to the soil, the higher the cumulative efflux was in the CB-NWR soil. In the SG-NWR, the cumulative efflux with the higher rewetting rates (≥ 50%) was very similar, but in contrast, the cumulative efflux at the lowest rewetting rate (25% WFPS) was significantly lower. In water-repellent soils, the cumulative efflux from both CB and SG soils was significantly lower ($p < 0.01$ for both CB and SG) than in the corresponding wettable soils, except in the CB soil with 25% rewetting rate (Fig. 4). The cumulative CO_2 efflux increased only slightly, but not significantly, with rewetting rates above 50% in CB-WR. In SG-WR, the cumulative efflux was similar independently of the rewetting rate; only at 25% rewetting rate was the cumulative efflux lower, but not significantly, than for the rest of rewetting rates.

In wettable soils, the cumulative CO_2 efflux was positively correlated to the water retained in the soil after wetting (Fig. 5). In the CB-NWR soil, a positive relationship between the cumulative CO_2 efflux and the amount of water retained in the soil after wetting was observed, but a surprisingly large efflux was observed in CB-WR with only a small amount of water retaining in the soil. For example, 8 cm^3 of retained water resulted in cumulative efflux of 5.8 mmol m^{-2}, a value similar to those observed in the wettable soils where more than 90% of water was retained in the soil after the wetting.

3.3 Effect of SWR on wetting, drainage and retained water

Soils of contrasting wettability (wettable WDPT < 5 s; extremely water-repellent WDPT > 3600 s) showed a very different response to wetting. All the water applied during the rainfall simulations infiltrated eventually into the soil, but for the wettable soils the infiltration was instant (WDPT < 5 s), while for the water-repellent soils, the average WDPT infiltration times were 7312 s and 10368 s for CB-WR and SG-WR respectively (Table 2). For the wettable soils, over 90% of the water added was retained in the soil, with only a small fraction of it draining to the container below the soil sample. In contrast, for the water-repellent soils, a significantly lower fraction of the total water applied (up to 6 and 10 % in the CB-WR and SG-WR respectively) was retained in the soils ($p < 0.001$ for both soils), with the remaining 94 to 90%, respectively, draining out of the soils (Table 3). Following wetting, SWC significantly increased accordingly with the rewetting rate in wettable soils, but in water-repellent soils, only small and non-significant differences were observed between different rewetting rates in CB and SG soils. An exception was SG-WR with 25% rewetting rate where SWC was significantly smaller than with the rest of rewetting rates.

4. Discussion

A distinctively lower CO_2 efflux response to the simulated rainfall was observed in the water-repellent soils compared to the typical 'Birch effect' seen in the wettable soils. Limited water infiltration and percolation patterns, characteristic of water-repellent soils, affected not only soil hydrology, but also led to reduced CO_2 efflux. SWR delays and limits infiltration of water to specific pathways of higher wettability or macropores created by roots, cracks, stones (Urbanek and Shakesby, 2009; Urbanek et al., 2015) and can result in rapid percolation of water downward to the subsoil via preferential flow paths (Ritsema and Dekker, 2000; Müller et al., 2014). Water typically travels in water-repellent soils through a narrow cross-section of soil pores, which results in the majority of the soil matrix remaining dry after rainfall (Hendrickx and Flury, 2001). Such rapid percolation through the water-repellent soil was also observed in this study. The water travelled only through a small fraction of the soil pores and within a short period of time (2 min of the start of wetting), up to 95% of the water applied drained into the container below the sample. The amount of water retained in the soil after wetting was minimal, with SWC ranging between 2–6% (Table 3). Only slight increases in the SWC were observed when higher amounts of water were applied, suggesting that the water moved through similar cross-sections of the pore-space regardless of the amount added to the surface. We expect that, in the water-repellent soils, infiltrating water released the soil CO_2 only from the affected sections of the soil matrix, resulting in the low CO_2 efflux observed in the headspace of the top and bottom chambers (Fig. 2 and 3). In contrast, in wettable soils, the large CO_2 pulse observed is likely to have resulted from the relatively uniform infiltration of water, which released the CO_2 out of the whole cross-section of the soil matrix (Fig. 6). Over 95% of the applied water was retained in the wettable soils. The more water that was applied, the higher the SWC was after wetting, resulting in higher CO_2 release from the soil.

The total CO_2 released from soils (also referred to as cumulative CO_2 efflux) was proportional to the water retained in the soil after the wetting in both wettable and water-repellent soils (Fig. 5). The almost immediate increase in CO_2 efflux with wetting of sterilised soil and its return to pre-wetting values after the wetting period suggests that this efflux increase has very unlikely been due to a rapid increase in microbial respiration, triggered by the reactivation of microbial activity after the sudden availability of water (Moyano et al., 2013). Several previous studies showed that the timescale for the reactivation of soil microbial activity under water-limiting conditions is a few hours (rather than seconds) after the input of water (Barnard et al., 2015; Salazar et al., 2018; Placella et al., 2012). The contribution of CO_2 from the chemical reaction with inorganic C (Rey, 2015) is also likely to be negligible as no inorganic C was detected in the soil. We expect that displacement of gas from soil pores by infiltrating water could be one of the sources, as suggested by Inglima et al. (2009) and Liu et al. (2002), but the amount of the cumulative efflux measured in the experiment was at least ten times higher than expected from the gas replacement. One possible mechanism responsible for the immediate CO_2 release after wetting may originate from the desorption of CO_2 molecules adsorbed to the surface of soil particles which are replaced by water molecules, as observed by Kemper et al. (1985). It has been previously suggested that the surface of SOM has the capacity to adsorb CO_2 (De Jonge & Mittelmeijer-Hazeleger, 1996) and that the adsorption capacity increases with the organic carbon content of the soil (Ravikovitch et al., 2005). Higher cumulative CO_2 effluxes measured from the soil with higher SOM content (SG soil) could thus be the result of increased adsorption capacity in comparison to CB soil. Other biochemical processes related to enzyme activity, as suggested by Fraser et al. (2015), could also have contributed to the overall CO_2 release.

Regardless of the source of the CO_2 it was very clear that the more water retained in the soil the higher was the cumulative CO_2 efflux. Unexpectedly high cumulative CO_2 efflux was observed with 75 and 100% rewetting rates in CB-WR and, to a lesser extent, in SG-WR despite the very low retention of water upon wetting. The cumulative efflux from the water-repellent soil was significantly lower than in CB-NWR ($p < 0.001$), but disproportionally high compared to the amount of retained water (Fig. 5). One possible explanation for such behaviour could be the localised increase in air pressure below the uneven wetting front (Wang et al., 2000) and along the preferential flow paths (Delahaye and Alonso, 2002), which could have facilitated gas movement out of the soil.

While the CO_2 release with wetting observed in this study is short-lived, its high magnitude is in line with previous studies (Marañón-Jiménez et al., 2011; Rey et al., 2017; Sánchez-García et al., 2020). In a recent laboratory study using intact core samples, Sánchez-García et al. (2020) estimated that the CO_2 peak during a wetting period accounted for nearly 80% of the total CO_2 released over the 5 h observation period. Similarly, Marañón-Jiménez et al. (2011) estimated that the degassing of soil pores was responsible for up to 64% of the total CO_2 released over the 2 h following wetting. It is common that studies investigating soil surface CO_2 emissions inherently identify the CO_2 effluxes with soil respiration (Maier et al., 2011) and do not account for the storage of gas in the soil matrix. According to Maier et al. (2010) up to 20% of the soil-produced CO_2 is not simultaneously emitted to the atmosphere, but it is instead stored in the pore-space and released during precipitation. As it has been shown in studies by White et al. (1977) and Wang et al. (2000), air entrapment is common in dry soils and could lead to fingered flow of rainwater, but SWR could further enhance air entrapment especially during high-intensity rainfall events. Our results, which show that some of the CO_2 is transported downwards upon wetting, support the idea of CO_2 storage (air entrapment) in the soil matrix and its release at a later stage. Whereas in the bottom chamber, a significantly lower peak than in the top chamber was observed in wettable soils ($p < 0.001$, $p = 0.001$ for CB-NWR and SG-NWR respectively), in water-repellent soils, the peak in both the top and bottom chambers showed similar magnitudes ($p = 0.525$, $p = 0.184$ for CB-WR and SG-WR respectively). This downward movement of gas suggests that under natural conditions, part of the stored CO_2 stored might be transported downwards upon wetting towards deeper areas of the soil profile until a favourable degassing route is found.

Another characteristic behaviour for the release of CO_2 from water-repellent soils was the second CO_2 pulse observed with higher rewetting rates in CB-WR, but not present during the rewetting of

SG-WR (Fig. 2 and 3). We expect that dual porosity of soil could have led to the second peak. The first peak likely originated from the release of CO_2 from macropores followed by the release of gas from inside the small aggregates, which could have had different wettability characteristics compared to the bulk soil (Urbanek et al., 2007). The overall porosity was similar in soils from both sites (56 and 59% in CB and SG soils respectively), but the CB soil had a higher silt fraction and visible aggregates, still present after sample preparation, suggesting dual porosity behaviour. Pore-size distribution influences water flow through the soil matrix with larger pores facilitating rapid infiltration (Kutílek, 2004; Smith et al., 2003) and, therefore, rapid movement of CO_2. The quick re-filling of larger pores first resulted in the spike observed in CB-WR, which is also supported by the quick and sharp peak (only 3 min after the start of wetting) in CB-NWR. The contribution of larger pores to the cumulative infiltration is especially pronounced in water-repellent soils, where preferential flow through larger pores has been estimated to contribute to up to 70 to 95% of the total infiltration through a water-repellent soil surface (Nyman et al., 2013). In the SG-NWR soil, the lower spike, but of longer duration (5.5 min after the start of wetting), suggests a relatively uniform re-filling of pores as a result of more homogeneous pore-size distribution.

This study has highlighted the substantial differences in CO_2 efflux upon rewetting between wettable and water-repellent soils. Given that the pre-treatment of soil material altered the internal soil structure and is likely to have affected their water flow patterns, the magnitude of the observed contrast in CO_2 efflux between wettable and water-repellent soils may differ somewhat to that of undisturbed field soils.

This study supports previous evidence that SWR potentially has a major impact on soil C dynamics (Goebel et al., 2011; Sánchez-García et al., 2020; Urbanek and Doerr, 2017), however, the effects that changes in hydrological properties caused by SWR might have on the C flux is an area that still requires further attention. Our results suggest that in highly water-repellent soils, pore-size distribution played a major role in the release of CO_2 after wetting, but how common this response is under different factors like soil type, rainfall intensity or the degree of water repellency remains unclear.

5. Conclusions

Our study shows that changes in the water-filled pore-space upon wetting, caused by SWR, reduces the short-term physical release of CO_2 in water-repellent soils. The high percolation concentrated along preferential paths resulted in low water retention in the soil and, therefore, low refilling of air-filled pores with infiltrating water. The CO_2 efflux was proportional to the amount of water retained in the soil after wetting. The pre-treatment of soil samples altered the soil structure so the CO_2 efflux in wettable and water-repellent soils might differ slightly in undisturbed soils. Our results also show that, upon wetting, some of the gas stored in the pore-space is displaced towards deeper areas of the soil profile and it is not released instantly. Under natural conditions, this downward flux might contribute to air entrapment below the wetting front, which could be released at a later stage.

Although SWR is a common characteristic of many soils, we are only beginning to understand the effects that water repellency-induced changes in soil hydrology might have on the overall soil C flux and current models remain unable to adequately reflect the dynamic nature of soil hydrological functions. Given that SWR is likely to become more common and severe with ongoing environmental change, future studies would be beneficial to further understand the longer-term effects of SWR on the overall soil C balance.

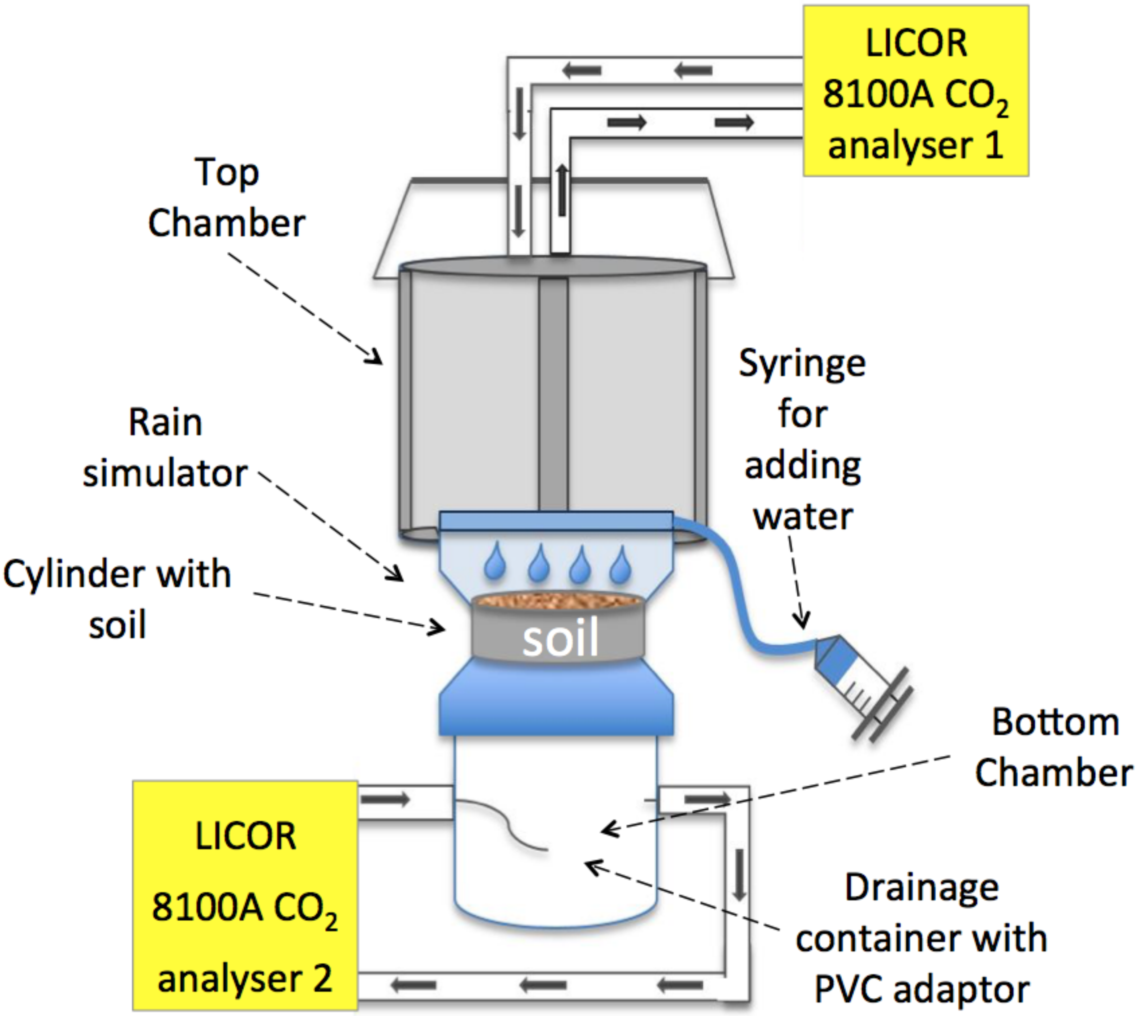

Fig. 1. Schematic illustration of rewetting and CO_2 analyser system.

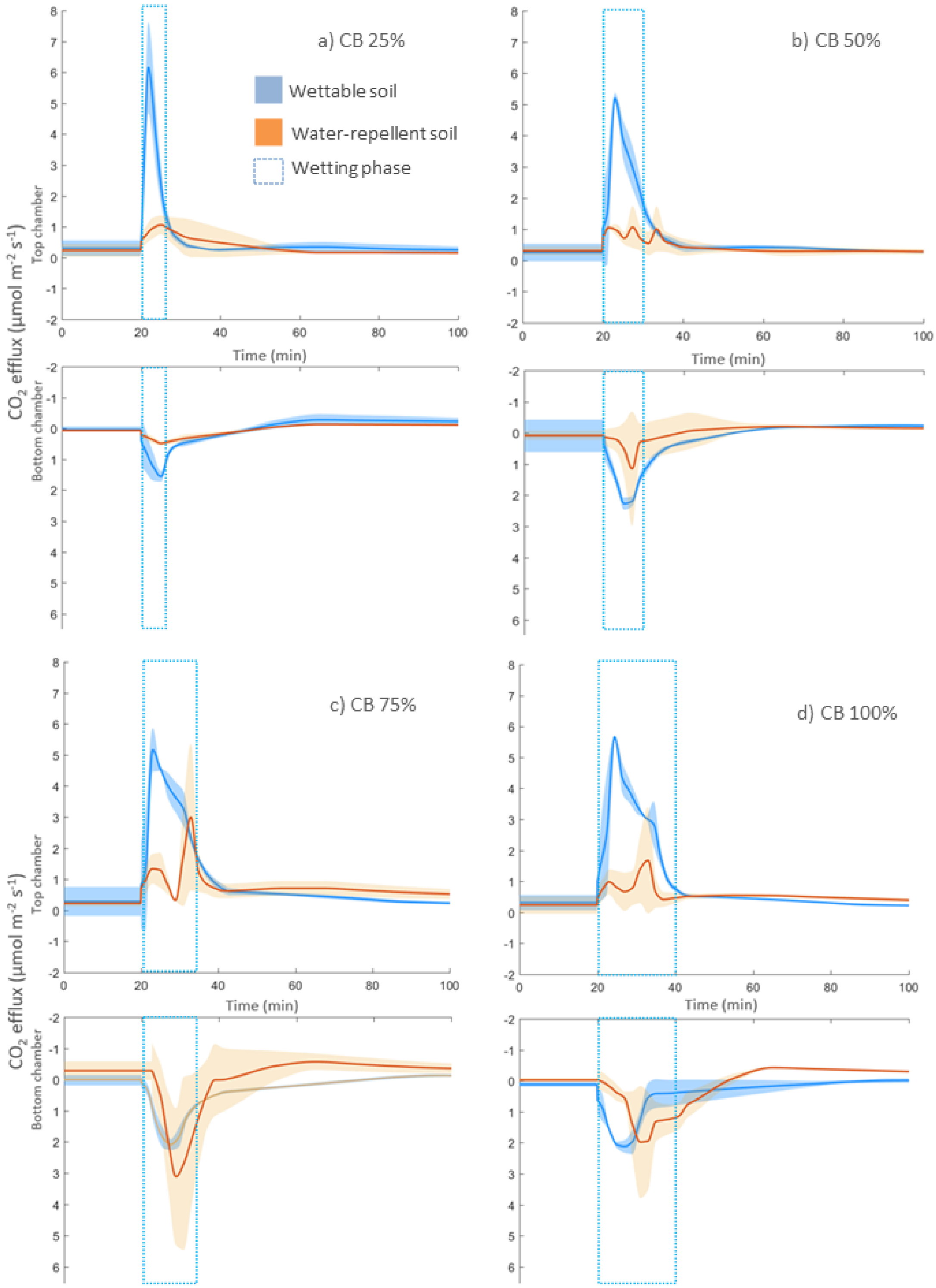

Fig. 2. Response of CO_2 efflux to wetting above and below the sample for autoclaved wettable (CB-NWR) and water-repellent (CB-WR) soil from CB under the 4 different rewetting rates (% of the water-filled pore-space). The orange line and shaded area represent the mean response (n = 3) with 95% confidence interval to the wetting of water-repellent soil and the blue line and shaded area represent the mean response (n = 3) with 95% confidence interval to the wetting of wettable soil.

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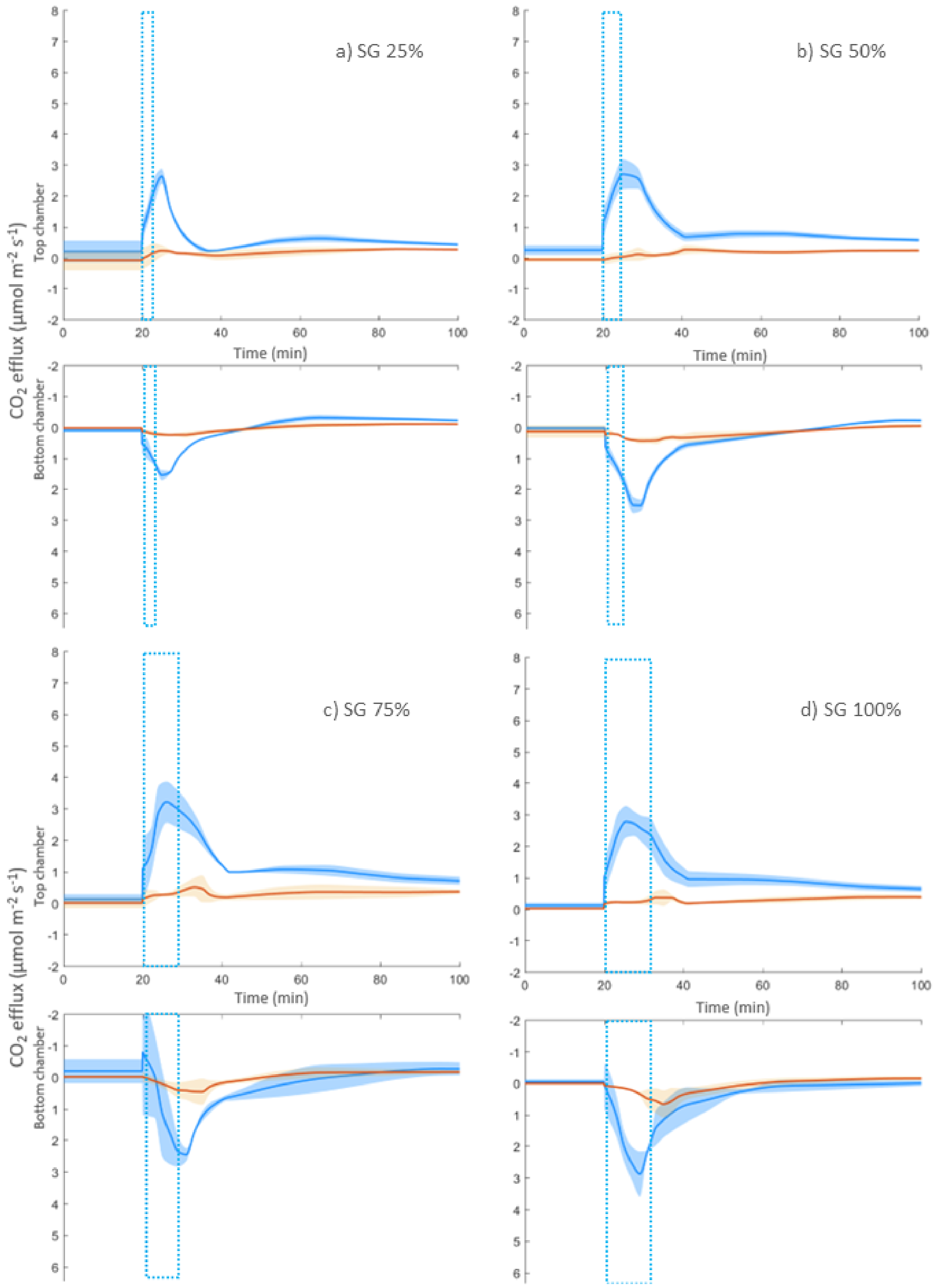
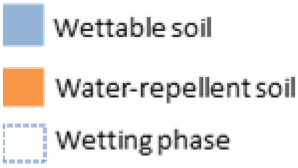


Fig. 3. Response of CO_2 efflux to wetting above and below the sample for autoclaved wettable (SG-NWR) and water-repellent (SG-WR) soil from SG under the 4 different rewetting rates (% of the water-filled pore-space). The orange line and shaded area represent the mean response (n = 3) with 95% confidence interval to the wetting of water-repellent soil and the blue line and shaded area represent the mean response (n = 3) with 95% confidence interval to the wetting of wettable soil.



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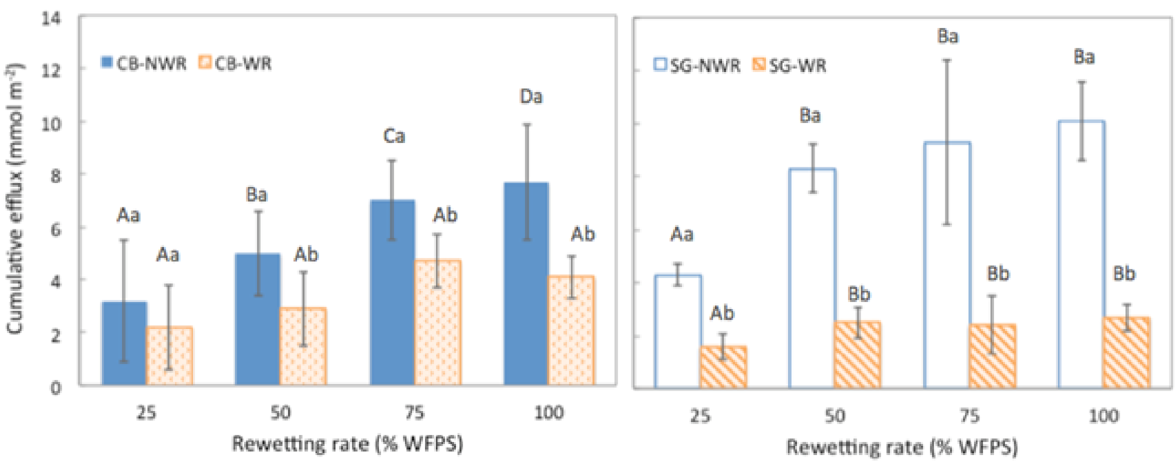

Fig. 4. Cumulative CO_2 efflux (top and bottom chambers combined) for wettable (CB-NWR and SG-NWR) and water-repellent (CB-WR and SG-WR) soils from CB and SG under the four different rewetting rates. Values are the mean (n = 3) with standard deviation bars. Different lowercase letters (a–b) within the same site and rewetting rate indicate significant differences between wettable and water-repellent soils at $p < 0.05$. Different uppercase letters (A–D) within the same site and soil wettability (wettable and water-repellent soil) indicate significant differences between rewetting rates at $p < 0.05$.

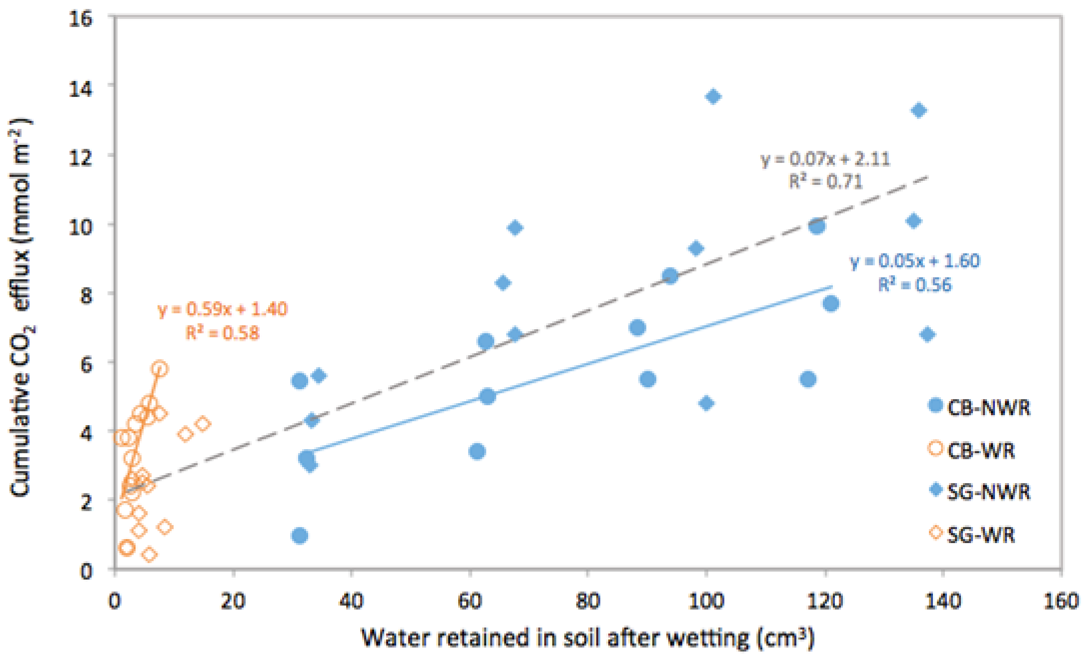

Fig. 5. Relationship between cumulative CO_2 efflux (top and bottom chambers combined) and water retained in the soil after wetting in wettable (CB-NWR and SG-NWR) and water-repellent (CB-WR and SG-WR) soils from CB and SG. Blue and orange solid lines represent the trendlines for CB-NWR and CB-WR respectively. The dashed line represents the trendline for the combined SG-NWR and SG-WR.

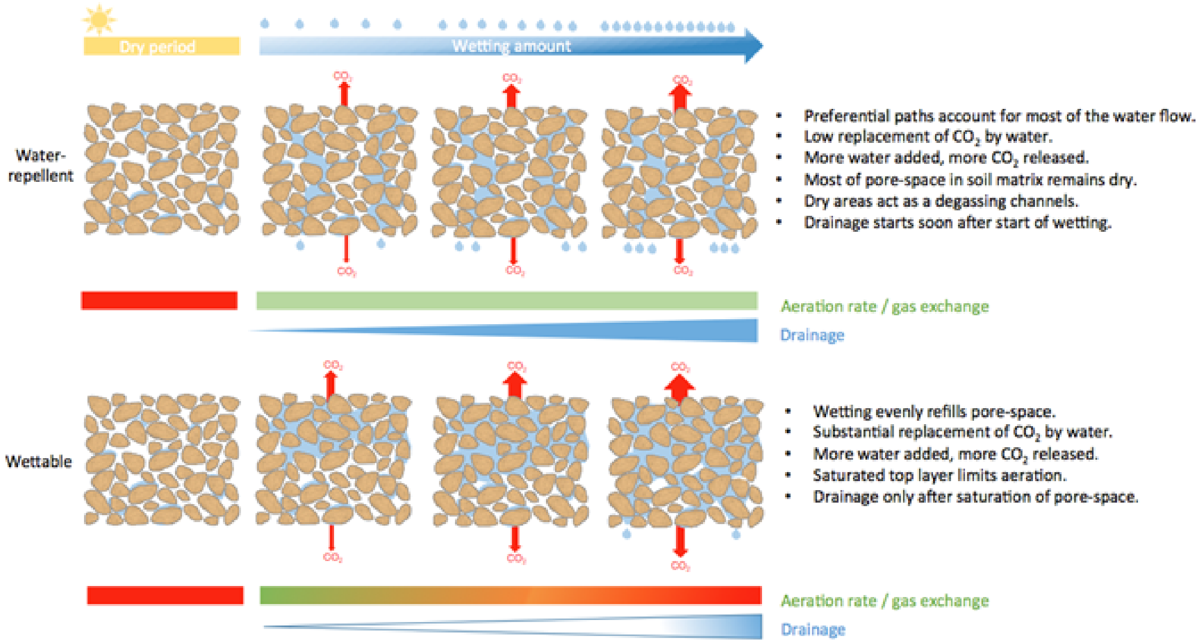

Fig. 6. Conceptual diagram of the development of wetting patterns with increasing rewetting rate in water-repellent and wettable soils and its effect on the release of CO_2 stored in the pore-space prior to wetting both upwards (emitted from soil surface) and downwards (contributing to CO_2 entrapment). Red arrows represent cumulative CO_2 efflux.

Table 1. General characteristics of the soils from the two study sites (CB: Cefn Bryn, SG: Southgate) before autoclaving.

	CB		SG	
% Soil organic matter (SOM)	11.1	(0.4)	32.1	(0.5)
Particle density (g cm^{-3})	2.31	(0.1)	2	(0.1)
% Porosity	56	(1.1)	59	(2.4)
pH (H_20)	4.8	(0.06)	6.4	(0.02)
pH ($CaCl_2$)	3.7	(0.04)	5.6	(0.02)
Particle size distribution				
% Sand	64.4	(0.03)	86.6	(1.86)
% Silt	33.6	(2.77)	12.3	(2.72)
% Clay	2.1	(0.18)	0.7	(0.17)
Texture	Sandy loam		Loamy sand	

Values represent the mean (n = 3) with standard deviation in brackets.

Table 2. Soil water repellency tests results (Doerr, 1998) before and after autoclaving both soils CB and SG at air-dry, intermediate and high gravimetric soil water content (SWC) (% g g^{-1}). Tests were done to assess optimal SWC for autoclaving to obtain wettable and water-repellent samples. Highlighted blue and pale orange values represent SWC values chosen for the experiment in order to obtain wettable and water-repellent samples respectively.

Soil	Before Autoclaving			After autoclaving			After autoclaving and oven drying (25 °C)		
	Water content (% g g^{-1})	WDPT (s)	SWR rating	Water content (% g g^{-1})	WDPT (s)	SWR rating	Water content (% g g^{-1})	WDPT (s)	SWR rating
CB	2.9	< 5	Wettable	6.1	256	Moderate	1.35	180	Moderate
	10.6	2120	Strong	8	> 3600	Extreme	1.28	4421	Extreme
	15.2	> 3600	Extreme	14	> 3600	Extreme	1.38	7312	Extreme
	38	< 5	Wettable	44.3	< 5	Wettable	1.57	< 5	Wettable
	49	< 5	Wettable	53.3	< 5	Wettable	1.45	< 5	Wettable
SG	4.7	< 5	Wettable	7.2	376	Moderate	3.09	423	Moderate
	11	44	Slight	14	> 3600	Extreme	3.35	8637	Extreme
	15.4	237	Moderate	19.8	> 3600	Extreme	3.42	10368	Extreme
	40.7	< 5	Wettable	40.1	11	Slight	7.1	128	Strong
	53	< 5	Wettable	52.2	< 5	Wettable	1.27	< 5	Wettable

Values represent the mean (n = 3).

Table 3. Average water retained in soil (expressed as volume in cm^3 and as % of total water applied) and gravimetric soil water content (SWC) (% g g^{-1}) after wetting for autoclaved wettable and water-repellent soils from CB and SG.

			Wettable			Water-repellent		
Soil	Rewetting rate (%)	Water added (ml)	Water retained in soil (cm^3)	Water retained in soil (%)	SWC (%)	Water retained in soil (cm^3)	Water retained in soil (%)	SWC (%)
CB	25	33	31.23 (0.05)	94.7 (0.07)	13.89 (0.02)	1.93 (0.85)	5.9 (0.85)	2.17 (0.34)
	50	65.5	62.33 (0.93)	95.2 (0.93)	26.33 (0.37)	3.23 (1.91)	4.9 (1.91)	2.69 (0.76)
	75	98	90.73 (2.84)	92.6 (2.84)	37.69 (1.14)	4.77 (2.63)	4.9 (2.63)	3.31 (1.05)
	100	131	118.97 (1.98)	90.8 (1.98)	48.99 (0.79)	4.1 (1.49)	3.1 (1.49)	3.04 (0.60)
SG	25	35	33.2 (0.30)	94.9 (0.3)	20 (0.15)	3.07 (1.00)	8.8 (1.0)	2.83 (0.50)
	50	70	67.27 (1.53)	96.1 (1.5)	37.03 (0.76)	6.9 (4.42)	9.9 (4.4)	4.75 (2.21)
	75	105	100.63 (2.18)	95.8 (2.2)	53.72 (1.09)	6.3 (1.23)	6 (1.2)	4.45 (0.61)
	100	140	136.53 (0.70)	97.5 (0.7)	71.67 (0.35)	9.33 (5.20)	6.7 (5.2)	5.97 (2.60)

Values represent the mean (n = 3) with standard deviation in brackets.

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