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Technical note: mesocosm approach to quantification of carbon dioxide fluxes across the vadose zone

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Abstract

Carbon dioxide (CO_2) fluxes in the vadose zone are influenced by a complex interplay of biological, chemical and physical factors. A soil mesocosm system was designed to assess the effect of agricultural practices on carbon fluxes within and out of the vadose zone at controlled environmental conditions. Carbon dioxide partial pressure (pCO_2), alkalinity, soil moisture and temperature were measured with depth and time, and DIC in the percolate was quantified using a sodium hydroxide trap. Results showed good reproducibility between two replicate mesocosms. The pCO_2 varied between 0.2–1.1 % and alkalinity was 0.1–0.6 meq L^{-1}. The measured effluent DIC flux was 185–196 mg L^{-1} m^{-2} and in the same range as estimates derived from pCO_2 and alkalinity in samples extracted from the side of the mesocosm column, and the water flux. The relatively small variation provides confidence that the mesocosm system is a promising tool for studying a range of processes in unsaturated environments. Meanwhile, high suction at the mesocosm bottom applied to reduce water ponding during intensive irrigation caused degassing of dissolved CO_2 from the water phase just below the outlet, leading to diffusion of dissolved CO_2 across the lower boundary. Though not influencing DIC flux measurements to the groundwater, this lead to a lowering of the pCO_2 in the stagnant water at the mesocosm bottom. A free-drainage boundary is suggested in order to avoid this effect.

1 Introduction

Dissolved carbon (C) leached from soils constitutes a significant fraction of the annual net carbon loss from croplands and grasslands but estimates are few (Kindler et al., 2011). A proportion of the C leached from soils is in the form of dissolved inorganic C (DIC). DIC in the soil water derives from the dissolution of biogenically produced carbon dioxide (CO_2) and carbonate minerals, and is controlled by the partial pressure of CO_2 (pCO_2), pH and temperature (Clark et al., 1997). However, our understanding of production and transport of CO_2 in the soil is incomplete (Jassal et al., 2005).

Increased understanding of the processes controlling DIC transport to aquifers can be obtained from measurements at field conditions or from studies under controlled conditions. Field studies have the advantage of being realistic but are also characterized by large uncertainty due to large spatial and temporal heterogeneity (e.g. Lange et al., 2009). Mesocoms studies under controlled conditions in the laboratory may be less realistic, but provide potential for a detailed study in a homogeneous environment and thereby offer better process understanding. Application of mesocosms for research on CO_2 fluxes in soil has mainly been focused on studies of gaseous effluxes (e.g. Lin et al., 1999; Cheng et al., 2000; Schnyder et al., 2003) while little attention has been paid to investigation of microbial respiration rates with depth in large-scale unplanted mesocosms (Lawrence and Hendry, 1995; Hendry et al., 2001) and to DIC leaching. Mesocosms provide useful environments for assessing biogeochemical processes in the root zone and in deeper soil layers under controlled conditions (Hendry et al., 2001). In this work, a soil mesocosm system was evaluated for its capability for producing realistic and reproducible inorganic C fluxes in the vadose zone of unplanted soil.

2 Methodology

2.1 Design and packaging of mesocosms

Two replicate mesocosms were constructed from transparent plexiglas cylinders with an outer diameter of 200 mm, inner diameter of 190 mm and a length of 850 mm (Fig. 1). The bottom of the mesocosms constituted of 30 mm thick polyethylene high density (PEHD) plates mounted with porous sintered PTFE filter discs of 70 mm diameter × 10 mm thickness (Prenart, DK) (Fig. 2a). A 70 mm diameter hole was drilled into the PEHD plate to create a 5 mm deep cavity beneath the filter disc. The cavity was

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connected with the outside of the mesocosm through a 3 mm wide channel. An o-ring smeared with silicone grease provided a gas- and water-tight seal between PEHD plate and cylinder wall.

Mesocosms were packed with air-dried and sieved (6 mm) A- and C-horizon soil material of coarse sandy texture (Table 1) from an agricultural field in Voulund, Denmark (56°2′ 35.7″ N, 9°8′ 101.1″ E) which has been maintained in agricultural rotation for > 100 yr. Before filling soil into the mesocosm, a 5 mm layer of an aqueous suspension of quartz flour was applied on top of the PEHD plate in order to optimize the hydraulic connection between the gravelly C horizon and the filter disc. Vacuum was applied to the mesocosm bottom outlet (Fig. 1) and the water in the suspension was sucked through the filter disc. When the quartz flour layer changed from wet to moist, a 30 mm layer consisting of a mixture of 0.5 kg dry quartz flour and 1 kg C horizon soil material was carefully added. The mesocosm C horizon was established in 10 sequential steps of ~ 30 mm each with a bulk density of $1.53 \pm 0.06\,\mathrm{g\,cm^{-3}}$ to a total C horizon height of ~ 480 mm. Next, a 300 mm A horizon with a bulk density of $1.47 \pm 0.05\,\mathrm{g\,cm^{-3}}$ was established using a similar procedure. This resulted in a diameter-to-length ratio of the packed soil column of 0.244 which is close to the suggested ratio of 0.25 for minimization of boundary effects (Lewis and Sjöstrom, 2010). In order to avoid soil compaction during wetting, each layer was compressed for 10 s by means of an adjustable weight pressure (Fig. 2b). The pressure exerted was slightly above the calculated weight of wet soil above the respective soil depth. The surface of each layer was scratched slightly to improve hydraulic contact between layers. The upper two soil layers were not exposed to the compression.

The mesocosms were equipped with the following samplers:

– Gas samplers were inserted at depths of 120, 210, 330, 430, 525, 645 and 730 mm. Gas samplers were assembled by mounting a loop of Accurell tubular membrane (Membrana, DE) on a y-piece connected to a Teflon tube. The tube was pushed through a gas tight 1/8 National Pipe Thread fitting in the mesocosm wall and was on the exterior connected to a three-way Luer-lock valve for syringe sampling outside the mesocosm wall (Fig. 2c and d). Additional gas sampling units were established at 40 and 60 mm depths by vertical insertion of Teflon tubes connected to a three-way Luer-lock valve and a syringe.

- EC-TM/5-TM sensors (Decagon Devices, USA) for measurement of the volumetric water content and temperature were installed at 65, 253, 315, 463, 623, 757 mm.
- Rhizon Flex samplers (Rhizosphere Research Products, NL) for water extraction were placed at depths of 65, 157, 253, 373, 460, 547, 660 and 755 mm.

Gas tightness of packed mesocosms was tested through pressure delivery to the column interior via a gas sampling port and application of leak detector spray to all fittings.

2.2 Experimental conditions of mesocosms

The filter disc at the bottom of the mesocosm was connected to a vacuum bottle in which the pressure was adjusted to prevent water logging in layers above the disc (Fig. 1). The required pressure varied from −0.1 to −0.75 bar relative to atmospheric pressure. Application of the filter disc prevented air flow out of the mesocosm as the pore size of the filter disc was sufficiently small to keep its pores water-filled at all times. The filter disc thus established an artificial, preclusion non-fluctuating, groundwater table that due to vertical air movement allowed for the reliable estimation of the water-mediated DIC flux to the groundwater.

The mesocosms were incubated in a climate chamber and maintained at mean daily air temperature of summer field conditions (18 °C) and night temperatures of 13 °C. Light with an intensity of ∼ 500 $\mu E\,m^{-2}\,s^{-1}$ was switched on 16 h day^{-1}. During incubation, the mesocosms were shaded from light with black plastic, leaving only the top uncovered, to avoid growth of algae on the mesocosm walls.

The mesocosms were irrigated using an adjustable peristaltic pump with 6 channels (no. 115, Ole Dich Instruments, DK). Each channel delivered a stable flow through a 2 mm diameter tube with a seal at the terminal end where a 25 cm section of the tube had ∼ 10 perforations to allow for scattered dripping of irrigation water onto the soil (Fig. 2e). The mesocosm soil columns were slowly watered with milli-Q water and the infiltration pattern showed homogeneous flow (Fig. 2f). Subsequent irrigation events were set as pulses providing 4.2–12.0 $mm\,m^{-2}\,h^{-1}$. After seven days, irrigation water was replaced by a 50 % strength Hoagland nutrient solution (Hoagland and Amon, 1950) with an alkalinity of 0.05 meq L^{-1} in order to avoid nutrient depletion of the soil under the frequent watering that is a prerequisite for establishment of vegetation in the mesocoms. Frequency and rate of irrigation was varied over the experimental period in order to outline the dependence of $p\mathrm{CO_2}$ on soil water content.

2.3 Measurements and calculations

2.3.1 Soil air

Samples of soil air were collected weekly in 1 mL aliquots from each port and were transferred to 5.9 mL septum vials (nr. 719W, Labco, UK). The $p\mathrm{CO_2}$ in the sample was measured on a 7890A GC System with FID detector in combination with a methanizer (Agilent Technologies, DK). Due to the importance of soil moisture content on $p\mathrm{CO_2}$and the immediate stimulation of microbial respiration by irrigation events, gas samples were collected > 12 h after an irrigation event.

2.3.2 Soil water

Soil water samples for determination of alkalinity were taken weekly, subsequent to $p\mathrm{CO_2}$ samples, transferred into closed glass vials and stored at 5 °C prior to analysis. Alkalinity was determined using the Gran Titration method (Gran, 1952).

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2.3.3 Soil moisture and temperature

Volumetric water content (VWC) and temperature within the mesocosms were logged at ten minute intervals using EM 50 loggers (Decagon Devices, USA) and a CR1000 logger (Campbell Scientific, UK). To increase measurement accuracy, sensors were calibrated to the A and C horizon conditions according to the guidelines of the manufacturers.

2.3.4 Dissolved inorganic carbon percolation

DIC in the percolating water was collected in 2 L vacuum flasks containing 15 mL 1 M carbon-free NaOH solution. The reaction that followed was

$$CO_2 + 2OH^- \rightarrow HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (1)$$

At a concentration of $OH^- > 0.1$ M (pH ∼ 13), bicarbonate is transformed instantaneously to carbonate (Pinsent et al., 1956). The added amount of NaOH ensured a pH > 10 in all drainage samples preventing degassing of CO_2 into the flask headspace. A carbon-free NaOH solution was obtained by adding solid NaOH (Merck, no. 106462) to degassed ("carbon-free") milliQ-water under a stream of N_2. The solution was sealed and stored in a desiccator containing a vial of soda lime. Prior to addition of the 1 M NaOH solution, vacuum flasks were evacuated and flushed with N_2.

DIC percolation was determined weekly on triplicates of percolate samples that were diluted ten times, transferred to sealed glass flasks and analyzed on a TOC_V CPH Analyzer (Shimadzu Suzhou Instruments, JP).

DIC percolation was also estimated using the measurements of CO_2 in the gas and water phase in the mesocosm. The [DIC] was calculated from the pCO$_2$, the alkalinity in soil solution and the temperature at the bottom of the mesocosms (∼60–73 cm) using PHREEQC software (Parkhurst and Appelo, 2011) and assuming chemical equilibrium. For the calculation, pCO$_2$ and temperature measurements were interpolated linearly. When low pCO$_2$was measured at the mesocosm bottom due to high water content (see

Sect. 3) the next sampler above was used to obtain the pCO_2 value. DIC concentrations were multiplied by the water flux to obtain the DIC percolation. One DIC percolation sample from each mesocosm was missing (day 39 and 74 for mesocosms 1 and 2, respectively). On those days the estimated values were used.

2.3.5 Statistical analysis

Linear regression analysis was conducted to test for the correlation between cumulative drainage (cDrainage) and cumulative DIC percolation (cDIC), as well as between measured and estimated cDIC (R version 2.12.0). The difference between the means of cDrainage and cDIC for the two replicate mesocosms was analyzed using a *t* test.

3 Results

The pCO_2at 25–67 cm depth followed identical patterns in both mesocosms and varied between 0.4–1.1 % with an overall declining trend (Fig. 3). The pCO_2 at the top (7 cm) was strongly reduced due to loss by diffusion and remained relatively stable at ~ 0.3 %. Significantly reduced pCO_2 was measured at the bottom at days 64 and 71 in mesocosm 1 and day 71 in mesocosm 2.

The VWC was 20–24 % in the A horizon and 7–15 % in the upper C horizon (37–56 cm) throughout the experimental period (Fig. 3). The VWC in the lower C horizon (67–76 cm) was 10–28 %, where high VWC was due to water logging at the mesocosm bottom after intensive irrigation events. Topsoil VWC decreased slightly during the experimental period, which resulted in decreased soil temperatures due to the higher heat capacity of water as compared to air. The temperature in the mesocosms declined with depth due to higher water contents in the A horizon and heat given off by the lamps in the climate chamber just above the mesocosm top.

Alkalinity was in the range 0.1–0.4 and 0.1–0.6 meq L^{-1} in mesocosms 1 and 2, respectively (Fig. 3). Observations of alkalinity from the same depth showed more vari-

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ation with time than the pCO_2 and VWC. Close inspection of Fig. 3 shows that the alkalinity in the upper C horizon was elevated compared to the A horizon and the lower C horizon, but decreased with depth towards the end of the experimental period.

The measured cDIC during the experimental period was 21.1–24.6 mg C (Fig. 4a) and equal to a DIC flux of 0.8–0.9 $g\,m^{-2}$. The estimated cDIC of 25.9–26.5 mg was only slightly higher than the measured values (Fig. 4a) and was closely correlated with the measured cDIC ($R^2 = 0.93$ and 0.98 for mesocosms 6 and 5, respectively). The cDrainage amounted to 149–157 mm and corresponded to 1.3 and 1.1 times the water-filled pore volumes for mesocosm 1 and 2, respectively. The measured cDIC and cDrainage were not significantly different between mesocosms ($p = 0.68$ and 0.99, respectively). The measured cDIC was highly correlated with cDrainage in both mesocosms ($R^2 = 0.94$–0.98) (Fig. 4b). On day 46 a three times higher drainage from mesocosm 1 caused a steep increase in cDIC, however the [DIC] remained nearly unchanged. The average [DIC] in the percolate from the mesocosms was 0.44–0.46 $mmol\,L^{-1}$.

4 Discussion

In general, there was a good agreement between observations from the two replicate mesocosms. Acknowledging the statistical limitation of having only two and not three or more replicates, analysis indicated that the measured cDIC was not significantly different between mesocosms and was highly correlated with the estimated cDIC. This suggests that DIC transport to aquifers, in agreement with theory (Appelo and Postma, 2005), can be described by soil gas pCO_2, soil water alkalinity and drainage flux, and underlines the reliability of the applied mesocosm system. Differences between the calculated and the measured cDIC could be related to disequilibrium between gaseous CO_2 and DIC or the fact that the measured pCO_2 was a “snap shot” of possible pCO_2 whilst the measured [DIC] in the percolate was the weekly average, as suggested by Walmsley et al. (2011). The good agreement between the two replicate mesocosms

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may reflect the careful homogenization of the soil and packaging of the mesocosms, as well as generally reliable sampling equipement and procedures.

Our results are in agreement with a reported pCO_2 of 0.5–1 % at 20 cm depth in a fallow silt loam field at soil temperatures of 5–20 °C and VWCs of 15–30 % (Buyanovsky and Wagner, 1983) and with 0.3–0.9 % pCO_2 at 15 cm depth in loam (temp. and VWC not reported) (Smith and Brown, 1933). Results were slightly higher than 0.2–0.3 % pCO_2 at 20 cm depth in bare Andisols at similar temperatures and VWCs (Yoshikawa and Hasegawa, 2000; Nakadai et al., 2002) and in large bare cylindrical mesocosms (2.4 m diameter and 4.6 m high) of sandy calcareous soil (Hendry et al., 2001); however, in these soils CO_2 was produced at depth. The alkalinity in the mesocosms was typical for streams fed by percolation water from western Danish sand soils (–0.23 to 1.55 meq L^{-1}) (Rebsdorf et al., 1991), but much lower than the reported mean of 5.2 meq L^{-1} in calcareous sand mesocosms (Hendry et al., 2001). However, alkalinity is soil type specific and pH dependent (Rebsdorf et al., 1991; Shin et al., 2011). The average [DIC] of 0.45 mmol L^{-1} in the percolation was lower than 1.7 mmol L^{-1} measured from fallow non-calcareous sand lysimeters (Verburg et al., 2004). However, day- and nighttime temperatures in the Verburg et al. study were 28 and 22 °C, respectively, which likely caused increased soil respiration, eventually leading to higher soil [DIC]. The average [DIC] in our study was similar to the [DIC] in the percolate from sandy forest soils with a topsoil pH of 3.8–4, but was far below the [DIC] in the percolate from croplands and grasslands (Kindler et al., 2011; Walmsley et al., 2011; Siemens et al., 2012). This underlines the crucial component of root respiration for soil pCO_2 and DIC export from soils. The pCO_2 in the mesocosms decreased over time, probably due to increased soil gas diffusivity with decreasing water content in the topsoil (Fig. 3) (Bouma and Bryla, 2000; Jassal et al., 2005; Zhang et al., 2010).

Alkalinity was higher in the C horizon than the A horizon, but decreased towards the bottom of the mesocosm. This suggests the presence of an acid-generating process at the mesocosm bottom that consumes alkalinity (Eq. 2), such as the precipitation of a gibbsite-type mineral (Eq. 3) as has been shown for several western Danish non-calcareous sandy sediments (Hansen and Postma, 1995; Kjøller et al., 2004).

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_{2\,(g)} + H_2O \quad (2)$$

$$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_{3\,(s)} + 3H^+ \quad (3)$$

A decrease in alkalinity throughout depth towards the end of the experiment (Fig. 3) was probably caused by the combined effect of flushing the mesocosms with irrigation water low in alkalinity, and a decreased release of alkaline ions into the soil solution through decreased weathering of soil minerals at lower pCO_2 (lower [carbonic acid]) (Andrews and Schlesinger, 2001; Karberg et al., 2005; Macpherson et al., 2008).

The accuracy of pCO_2 and alkalinity measurements at the mesocosm bottom was crucial because both were used for estimating the DIC percolation. The reason for the decreased pCO_2 at the mesocosm bottom on days 64 and 71 is not clear but might be related to prolonged periods of high VWC (~ 25 %) (Fig. 3). It is well known that the pCO_2 decreases at high water content due to the inhibition of respiration as the pore spaces become saturated with water and depleted of oxygen (Linn and Doran, 1984; Bekele et al., 2007). However, despite lower CO_2 production at high VWC at depth in the mesocosms, vertical diffusion should still have settled pCO_2 at fairly equal level, as is seen in the field (Hamada and Tanaka, 2001; Schulz et al., 2011; Wang et al., 2013).

Hence we reason that the explanation for low pCO_2 lies in the combined action of the high applied suction (−0.7 atm) beneath the filter disc and considerable waterlogging above the filter disc. The lowering in total pressure (i.e., to 0.3 atm) across the filter disc may have given rise to gas phase formation because the sum of the partial gas pressures of N_2, O_2, CO_2, Ar, etc. then obviously must have exceeded that of the total pressure. The gas phase may have formed within the lower part of the filter disc itself and/or in the cavity immediately below the disc. This would allow dissolved CO_2 to degas into the newly formed gas phase and hence lead to a drop in the dissolved concentration of CO_2. In that case diffusion of CO_2 through the ponded water and across the filter disc would lead to a lowering of the pCO_2 in the stagnant water at the mesocosm bottom, i.e. above the filter disc. The effect was only visible when significant ponding occurred due to the several-centimeters distance from the filter disc to the lowest gas sampler. Also, bubbles were observed sporadically in the tubing to the effluent bottle, supporting gas phase formation in response to the drop in total pressure. While the magnitude of the diffusional efflux of CO_2 across the filter disc is expected to be small due to the low diffusion coefficient for CO_2 in water, the flux might have slightly lowered total CO_2 within the mesocosm. Meanwhile, the degassing of CO_2 had little effect on the measurement of CO_2 flux to the aquifer, as the latter was determined by the amount of carbon trapped in the NaOH solution of the effluent flask, independently on whether the carbon arrives to the trapping solution in its dissolved or gaseous form. In the light of high nutrient concentrations in the irrigation water and possible interaction with soil mineral equilibria and cation exchange, the lowering of total pressure beneath the filter disc might also cause other complications such as clogging of the filter disc by precipitation. As high irrigation amounts are needed in order to flush the mesocosms with by at least one water-filled pore volume the application of lower suction at the lower boundary is not an option if an experiment is to be carried out within reasonable time. We suggest the use of a free-drainage boundary in order to avoid complications arising at the filter disc, though this implies dealing with vertical movement of soil air induced by a fluctuating groundwater table which similarly can complicate the interpretation of measured CO_2 fluxes.

Application of the filter disc caused a shallower vadose zone than at the site of soil collection. This implies a lower capacity for downward diffusing CO_2 and some difference in the pCO_2 at the artificial and at the true groundwater table can therefore be expected to arise from the experimental setup alone. Carbon dioxide production is not thought to be influenced by the position of the groundwater table as most respiration is generated in the topsoil where organic matter is abundant (Table 1) (reviewed in Kuzyakov, 2006 and Trumbore, 2006).

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5 Conclusions

Mesocosms studies are superior to field studies for achieving detailed mechanistic and process-oriented information. This study demonstrates that well-designed mesocosms can provide reproducible measurements of inorganic carbon fluxes in the vadose zone that are similar to field measurements. Our results show that DIC transport to aquifers in fallow soils is well described by soil gas pCO_2, soil water alkalinity and drainage flux. Mesocosms appear to be suited for more process-related research on CO_2 fluxes in the vadose zone, potentially involving plants and various soil managements that can aid to fill the gaps in current our understanding.

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Table 1. Soil properties.

Parameter	Horizon A (0–300 mm)	Horizon C (300–780 mm)
Organic C content (%)[2]	2.8	0.04
C / N ratio[2]	18.9	4.5
Plant-available P ($\mu g\,g^{-1}$)[2]	34.8	3.5
Bulk density ($g\,cm^{-3}$)[1]	1.47	1.54
Porosity (%)[1]	45	42
Clay and silt content (%)[2]	4.0	0.2
Cation exchange capacity (meq/100 g)[2]	0.87	0.21
pH[2]	6.0	6.6

[1] Measured from samples collected from the mesocosms.
[2] Measured prior to filling of the mesocosms.

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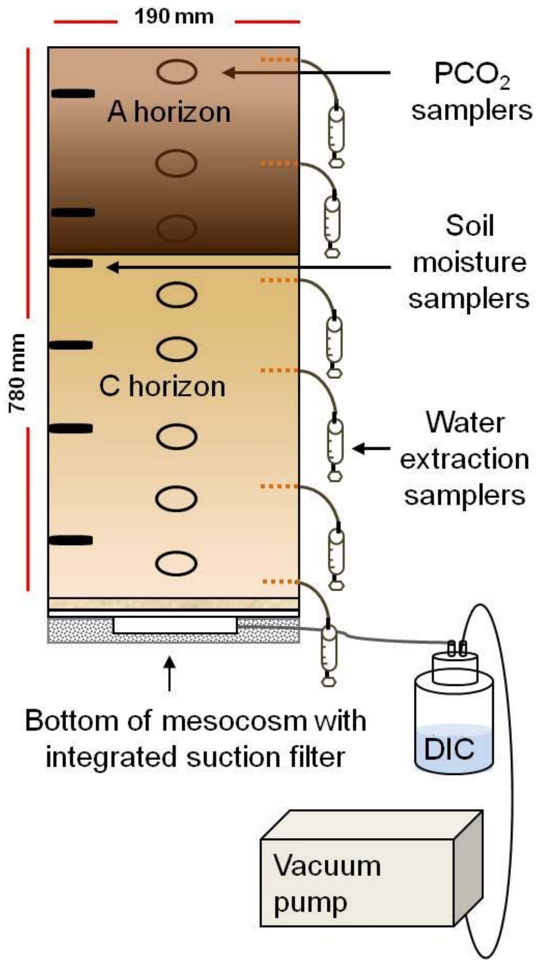

Fig. 1. Sketch of mesocosm with integrated sampling equipment and collection system for DIC at the bottom.

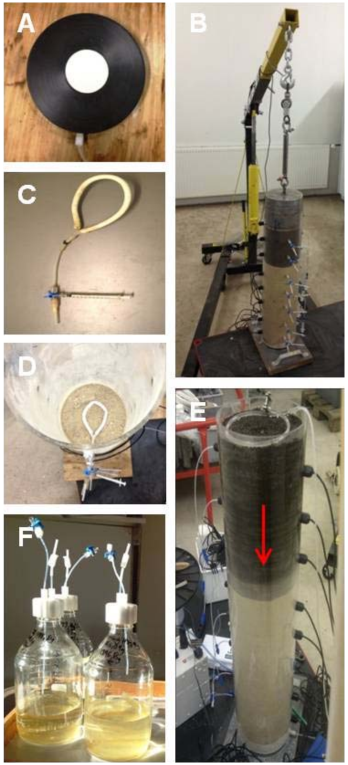

Fig. 2. Mesocosm construction for measurement of CO_2 fluxes in the vadose zone. **(A)** PEHD plate as bottom of the mesocosms with integrated filter disc. A 3 mm wide hole (not visible) connects a narrow cavity under the filter disc with the mesocosm outlet, allowing for controlled suction pressure at the mesocosm bottom. **(B)** Each layer is compacted by a weight that is above the wet tare of the overlying soil column at the given depth. **(C)** Gas sampler. **(D)** Gas sampler built into a 30 mm layer in the mesocosm. **(E)** Mesocosm with irrigation tubing during watering of a newly constructed, dry mesocosm. Red arrow indicates infiltration front. **(F)** Vacuum flasks for effluent collection.

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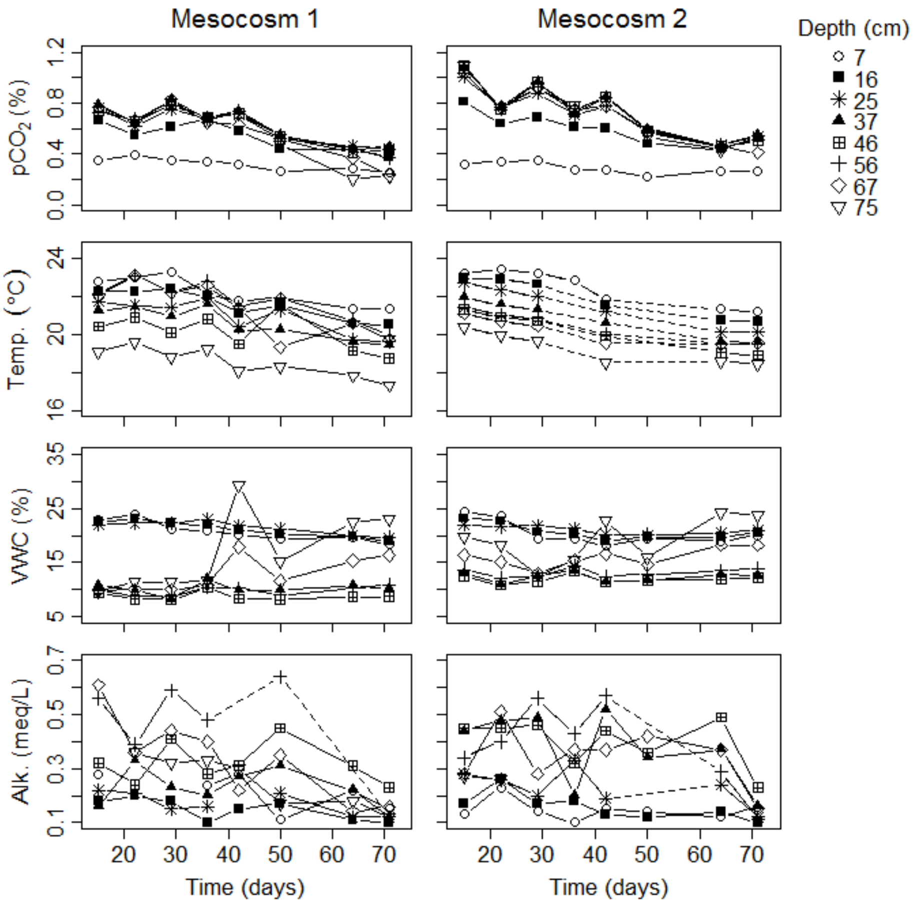

Fig. 3. Time course of interpolated pCO_2, temperature, volumetric water content (VWC) and alkalinity on measurement days throughout depth in the mesocosms. Stippled lines indicate missing recordings/measurements.

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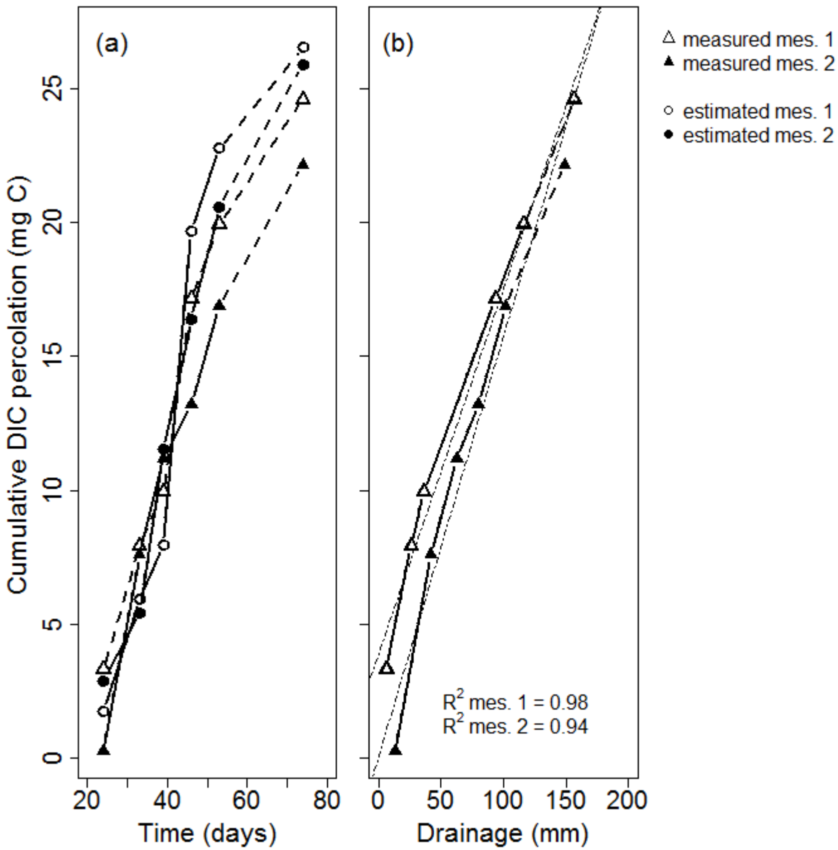

Fig. 4. Measured and estimated cumulative DIC percolation as a function of time **(a)** and measured cumulative DIC percolation as a function of cumulative drainage **(b)**. DIC percolation was estimated from alkalinity, $p\mathrm{CO}_2$ and water flux. Bold stippled lines indicate closure of the outlet. Narrow dot-dashed lines in **(b)** are regression lines.