



Technical Note: Mesocosm approach to quantify dissolved inorganic carbon percolation fluxes

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Abstract. Dissolved inorganic carbon (DIC) fluxes across the vadose zone are influenced by a complex interplay of biological, chemical and physical factors. A novel soil mesocosm system was evaluated as a tool for providing information on the mechanisms behind DIC percolation to the groundwater from unplanted soil. Carbon dioxide partial pressure ($p\text{CO}_2$), 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 $p\text{CO}_2$ varied between 0.2 and 1.1 %, and the alkalinity was 0.1–0.6 meq L⁻¹. The measured cumulative effluent DIC flux over the 78-day experimental period was 185–196 mg L⁻¹ m⁻² and in the same range as estimates derived from $p\text{CO}_2$ and alkalinity in samples extracted from the side of the mesocosm column and the drainage flux. Our results indicate that the mesocosm system is a promising tool for studying DIC percolation fluxes and other biogeochemical transport processes in unsaturated environments.

constitutes a significant fraction of the annual net C loss from croplands and grasslands (Kindler et al., 2011), suggesting a need for wider quantification of the DIC percolation flux from these systems. Dissolved inorganic carbon in the soil water derives from the dissolution of biogenically produced CO₂ and carbonate minerals and is controlled by the partial pressure of CO₂ ($p\text{CO}_2$), pH and temperature (Clark et al., 1997). However, our understanding of soil water DIC formation is incomplete due to incomplete understanding of production and transport of CO₂ in the soil (Jassal et al., 2005), which determine the $p\text{CO}_2$ at any given time and space.

A better understanding of the processes controlling DIC formation and 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). Soil column studies under controlled conditions in the laboratory may be less realistic, but provide potential for a detailed study in a homogeneous environment and may thereby offer better process understanding. In the following, we collectively refer to incubated and non-incubated filled soil columns and monoliths as mesocosms. Process understanding from mesocosm experiments may be double-checked through subsequent modeling studies for which homogenous and controlled conditions provide the ideal study frame.

1 Introduction

The global flux of carbon dioxide (CO₂) from the soil to the groundwater as dissolved inorganic carbon (DIC) is estimated at 0.2 Gt carbon (C) yr⁻¹ and is much less than the upward flux of CO₂ from the soil to the atmosphere of 59–76.5 Gt C yr⁻¹ (Kessler and Harvey, 2001; Raich and Potter, 1995; Houghton, 2007). However, DIC leached from soils

Application of mesocosms for research on CO₂ 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 the pCO₂ 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 simple and economical soil mesocosm system consisting of carefully filled, homogenized, sieved soil was evaluated for its capability of producing reliable DIC percolation fluxes to aquifers beneath unplanted soil. We compare DIC fluxes obtained from direct measurements with DIC fluxes indirectly determined via measurements of pCO₂, pore water alkalinity and drainage flux.

2 Methodology

2.1 Design and construction 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 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 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 more than 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. Just before the quartz flour layer became dry, a 30 mm layer of a 0.5:1.0 mixture (*w/w*) of dry quartz flour and C horizon soil material was added. The mesocosm C horizon was established in 10 sequential steps of ~30 mm each with a bulk density of $1.53 \pm 0.06 \text{ g cm}^{-3}$ to a total C horizon height of ~480 mm. Next, a 300 mm A horizon with a bulk density of $1.47 \pm 0.05 \text{ g cm}^{-3}$ 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

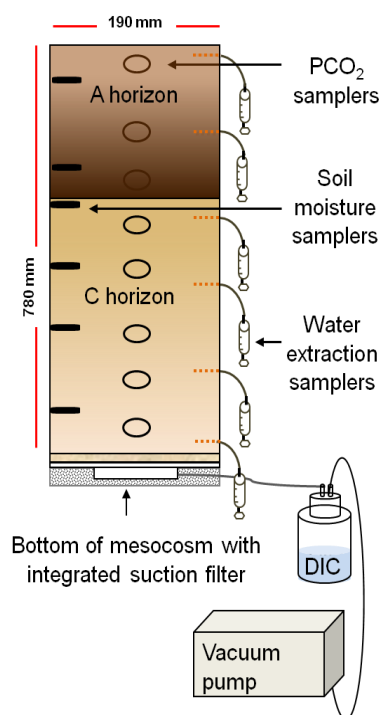


Fig. 1. Sketch of mesocosm with integrated sampling equipment and collection system for DIC at the bottom.

Sjöström, 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 Accurel 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.

Table 1. Soil properties. The soil bulk density and porosity were determined from samples collected from the mesocosms. All remaining parameters were measured prior to filling of the mesocosms.

Parameter	Horizon	
	A (0–300 mm)	C (300–780 mm)
Organic C content (%)	2.8	0.04
C/N ratio	14.9	4.5
Plant-available P ($\mu\text{g g}^{-1}$)	34.8	3.5
Bulk density (g cm^{-3})	1.47	1.53
Porosity (%)	45	42
Clay and silt content (%)	4.0	0.2
Cation exchange capacity ($\text{meq } 100 \text{ g}^{-1}$)	2.59	0.34
pH	6.0	5.4

- 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, non-fluctuating groundwater table required to estimate the water-mediated DIC flux to the groundwater reliably.

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 $\sim 500 \mu\text{E m}^{-2} \text{s}^{-1}$ was switched on 16 h d^{-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 six 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). Prior to the experiment, the mesocosm soil was slowly pre-wetted with Milli-Q water; the infiltration pattern showed homogeneous flow (Fig. 2e). During the experiment, irrigation events were set as pulses providing $4.2\text{--}12.0 \text{ mm m}^{-2} \text{ h}^{-1}$. Generally high irrigation rates were applied to ensure downwards percolation. Seven days into the experiments, the irrigation water was replaced by a 50 % strength Hoagland nu-

trient solution with an alkalinity of 0.05 meq L^{-1} (Hoagland and Amon, 1950) in order to avoid nutrient depletion of the soil under the high irrigation regime applied. Frequency and rate of irrigation was varied over the experimental period (78 days) in order to outline the dependence of the $p\text{CO}_2$ on the 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 (no. 719W, Labco, UK). The $p\text{CO}_2$ in the sample was measured on a 7890A GC System with flame ionization detector in combination with a methanizer (Agilent Technologies, DK). Due to the importance of soil moisture content on $p\text{CO}_2$ and the immediate stimulation of microbial respiration by irrigation events, gas samples were collected more than 12 h after an irrigation event.

2.3.2 Soil water

Soil water samples for determination of alkalinity were taken weekly, subsequent to $p\text{CO}_2$ samples, transferred into closed glass vials and stored at 5°C prior to analysis. Alkalinity was determined using the Gran titration method (Gran, 1952).

2.3.3 Soil moisture and temperature

Volumetric water content (VWC) and temperature within the mesocosms were logged at 10 min 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

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

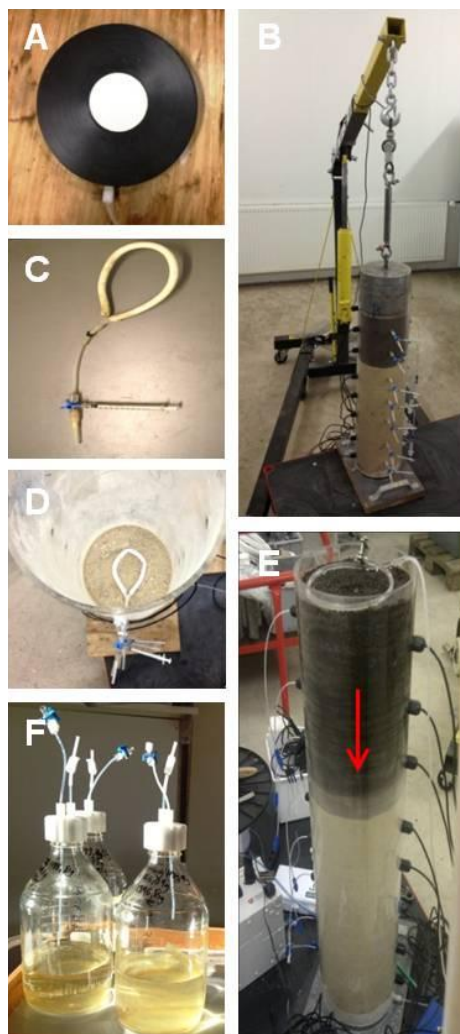


Fig. 2. Mesocosm construction for measurement of DIC fluxes in the vadose zone. **(A)** PEHD plate as bottom of the mesocosms with integrated filter disc. A 3 mm-wide hole (not visible) connects a narrow cavity under the filter disc with the mesocosm outlet, allowing for controlled suction pressure at the mesocosm bottom. **(B)** Each 30 mm soil 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 soil 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.

(Fig. 2f). The reaction that followed was



At a concentration of $\text{OH}^- > 0.1 \text{ M}$ ($\text{pH} \sim 13$), bicarbonate is transformed instantaneously to carbonate (Pinsent et al., 1956). The added amount of NaOH ensured a $\text{pH} > 10$ 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”) Milli-Q 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 .

Dissolved inorganic carbon percolation was determined weekly on triplicates of percolate samples that were diluted 10 times, transferred to sealed glass flasks and analyzed on a TOC_V CPH Analyzer (Shimadzu Suzhou Instruments, JP). Dissolved inorganic carbon percolation was also estimated using the measurements of CO_2 in the gas and water phase in the mesocosm. Dissolved inorganic carbon concentrations ([DIC]) were calculated from the pCO_2 , the alkalinity in soil solution and the temperature at the bottom of the mesocosms ($\sim 60\text{--}73 \text{ cm}$) using PHREEQC software (Parkhurst and Appelo, 2011), and assuming chemical equilibrium. For the calculation, pCO_2 and temperature measurements were interpolated linearly to match the depths of alkalinity measurements. When low pCO_2 was measured at the mesocosm bottom due to high water content (see Results), the next sampler above was used to obtain the pCO_2 value. The [DIC] was 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 the cumulative drainage and cumulative DIC percolation, as well as between the estimated and directly measured cumulative DIC percolation (R version 2.12.0). A t test was applied to analyze the differences between the means of cumulative drainage and cumulative DIC percolation for the two replicate mesocosms and between the slopes of estimated vs. measured cumulative DIC percolation in the combined data set and the 1 : 1 line.

3 Results

The pCO_2 at 25–67 cm depth followed identical patterns in both mesocosms and varied between 0.4 and 1.1 %, with an overall declining trend over time (Fig. 3). The pCO_2 at the top (7 cm) was much lower than in deeper soil layers due to loss by diffusion and remained relatively stable at $\sim 0.3 \%$. Also, in brief periods of time, the pCO_2 was significantly lower at the bottom of mesocosms 1 (at 64 and 71 days) and 2 (at 71 days) than in the soil layers above.

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

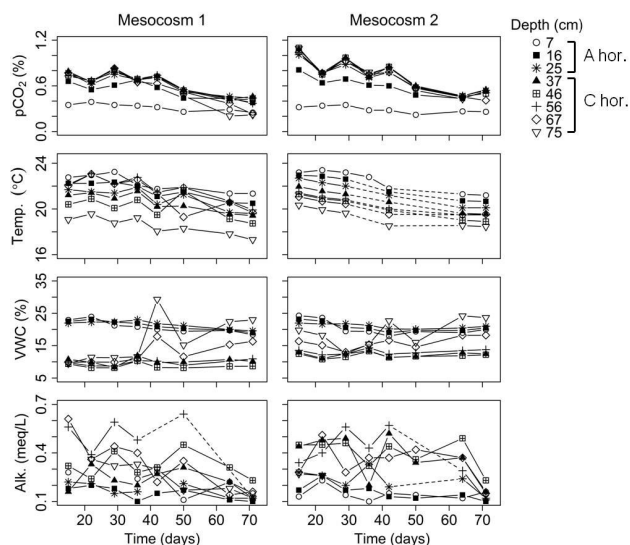


Fig. 3. Time course of linearly interpolated $p\text{CO}_2$, temperature, volumetric water content (VWC) and alkalinity (Alk.) on measurement days throughout depth in the mesocosms. Dashed lines indicate missing samples/measurements.

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.

The alkalinity was in the range $0.1\text{--}0.6\text{ meq L}^{-1}$ (Fig. 3). Observations of alkalinity from the same depth showed more variation with time than the $p\text{CO}_2$ 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 directly measured cumulative DIC percolation during the experimental period was $21.1\text{--}24.6\text{ mg C}$ (Fig. 4a) and corresponds to a cumulative DIC percolation flux of $0.8\text{--}0.9\text{ g m}^{-2}$. The estimated (i.e., indirectly determined) cumulative DIC percolation of $25.9\text{--}26.5\text{ mg}$, calculated from $p\text{CO}_2$, pore water alkalinity and water flux, was only slightly higher than the measured values (Fig. 4a) and was closely correlated with the measured cumulative DIC percolation ($R = 0.99$ and 0.98 for mesocosms 1 and 2, respectively, and $p < 0.001$ for both mesocosms). However, the slope of the regression for the estimated vs. the directly measured cumulative DIC percolation in the combined data set was significantly different from the 1:1 line ($p < 0.001$, Fig. 4c). The cumulative drainage was $149\text{--}157\text{ mm}$ and corresponded to 1.3 and 1.1 times the water-filled pore volumes for mesocosms 1 and 2, respectively. The measured cumulative DIC percolation and cumulative drainage were not significantly different between mesocosms ($p = 0.68$ and 0.99 , respectively). The measured cumulative DIC percolation was

highly correlated with the cumulative drainage in both mesocosms ($R = 0.97\text{--}0.99$) (Fig. 4b). On day 46 a three times higher drainage from mesocosm 1 caused a steep increase in the cumulative DIC percolation. However, the [DIC] remained nearly unchanged. The average [DIC] in the percolate from the mesocosms was $0.44\text{--}0.46\text{ mmol L}^{-1}$.

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, statistical analysis indicated that the measured cumulative DIC percolation was not significantly different between mesocosms and was highly correlated with the estimated cumulative DIC percolation. This suggests that DIC transport to aquifers, in agreement with theory (Appelo and Postma, 2005), can be described by soil gas $p\text{CO}_2$, soil water alkalinity and drainage flux, and underlines the gas tightness and reliability of the applied mesocosm system. Differences between the estimated and the measured cumulative DIC percolation could be related to disequilibrium between gaseous CO_2 and DIC or the fact that the measured $p\text{CO}_2$ was a “snap shot” of possible $p\text{CO}_2$ whilst the measured [DIC] in the percolate was the weekly average, as suggested by Walmsley et al. (2011). The good agreement between results from the two mesocosms may reflect the careful homogenization of the soil and filling of the mesocosms, as well as generally reliable sampling equipment and procedures. Our results suggest that the mesocosm system is well suited for investigation of the effect of different agricultural practices such as liming, fertilization, irrigation or cropping on the DIC percolation flux.

Our results are in agreement with a reported $p\text{CO}_2$ of $0.5\text{--}1\%$ at 20 cm depth in a fallow silt loam field at soil temperatures of $5\text{--}20^\circ\text{C}$ and VWCs of $15\text{--}30\%$ (Buyanovsky and Wagner, 1983) and with $0.3\text{--}0.9\%$ $p\text{CO}_2$ at 15 cm depth in loam (temp. and VWC not reported) (Smith and Brown, 1933). 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). The average [DIC] in our study was similar to the [DIC] in the percolate from sandy forest soils with a topsoil pH of $3.8\text{--}4$, 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 indicates that a higher pH in cropland soil and a lower $p\text{CO}_2$ in the absence of roots are acting in opposite directions in terms of DIC formation. The $p\text{CO}_2$ decrease over time was probably due to the concurrent 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).

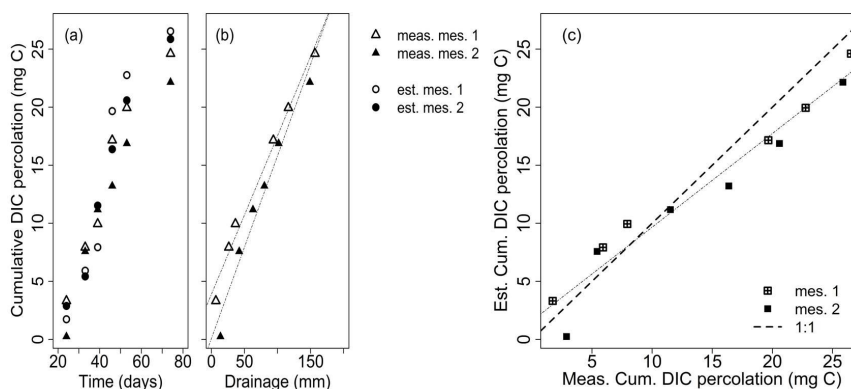
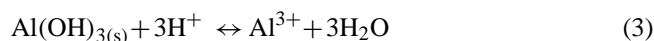
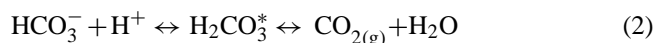


Fig. 4. Directly measured and estimated cumulative DIC percolation vs. time (a), directly measured cumulative DIC percolation vs. cumulative drainage (b) and estimated vs. directly measured cumulative DIC percolation (c). The estimated DIC percolation was calculated from alkalinity, $p\text{CO}_2$ and water flux. Narrow dot-dashed lines in (b) and (c) are regression lines; in (c) the regression comprises both mesocosms.

The alkalinity increased from the A to the C horizon, in accordance with mineral dissolution by carbonic acid. However, the alkalinity 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), where $\text{H}_2\text{CO}_3^* = \text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3$), such as the precipitation of a gibbsite-type mineral (Eq. 3). The latter has been shown for several western Danish non-calcareous sandy sediments (Hansen and Postma, 1995; Kjølner et al., 2004).



The accuracy of $p\text{CO}_2$ and alkalinity measurements at the mesocosm bottom was crucial because both were used for estimating the DIC percolation flux. The reason for the decreased $p\text{CO}_2$ at the mesocosm bottom on days 64 and 71 is not clear but might be related to prolonged periods of high VWC ($\sim 25\%$) (Fig. 3). It is well known that the $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ lies in the combined action of the high applied suction (-0.7 atm relative to atmospheric pressure) beneath the filter disc and considerable waterlogging above the filter disc. The lowering in total pressure from 1 atm above to 0.3 atm below the filter disc potentially caused gas-phase formation because the sum of the partial gas pressures of N_2 , O_2 , CO_2 and Ar then obviously must have far exceeded the total pressure;

the partial pressure of N_2 alone is 0.79 atm when in equilibrium with atmospheric air at 1 atm. The gas phase may have formed within the filter disc itself and/or in the cavity immediately below the disc. This would allow dissolved CO_2 to de-gas 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 $p\text{CO}_2$ in the stagnant water at the mesocosm bottom (i.e., above the filter disc). The effect was only visible when ponding submerged 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. The diffusional efflux of CO_2 across the filter disc might have slightly lowered total CO_2 within the mesocosm, though probably to a minor extent only. Meanwhile, the degassing of CO_2 had little effect on the measurement of the DIC percolation flux, 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 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. Since 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. The latter can similarly complicate the interpretation of the measured DIC fluxes and $p\text{CO}_2$ due to hence induced advective gas transport.

The mesocosm column height of course constrains the emulated vadose zone thickness; in our case the mesocosm

height (0.8 m) was much lower than the vadose zone thickness at the site of soil collection (4–6 m). This implies a lower capacity for downward diffusing CO₂, and some difference in the *p*CO₂ at the artificial (mesocosm) and at the true (field site) groundwater table can therefore be expected to arise from the experimental setup alone. However, carbon dioxide production in the mesocosms is not thought to have been influenced by the mesocosm height as most respiration is generated in the topsoil where organic matter is abundant (Table 1) (Kuz'yakov, 2006; Trumbore, 2006).

The installation of monitoring equipment along the depth of the mesocosms is expected to have caused little alteration to the soil integrity and bulk density as the combined volume of all samplers ($\sim 9.7 \times 10^{-2}$ L) constituted only $\sim 0.5\%$ of the volume of the soil-filled mesocosm (19.8 L).

5 Conclusions

In this study, a novel mesocosm system was evaluated for the measurement of DIC percolation fluxes from the vadose zone. Our results show that measured DIC percolation fluxes can be predicted by indirect estimates derived from soil gas *p*CO₂, soil water alkalinity and drainage flux. Hence, the mesocosm system appears to be a promising tool for more process-related research on DIC percolation fluxes across the vadose zone, potentially involving plants and various soil managements.

Supplementary material related to this article is available online at <http://www.biogeosciences.net/11/1077/2014/bg-11-1077-2014-supplement.pdf>.

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