New Sensor Technology for Field-Scale Quantification of Carbon Dioxide in Soil

Detlef Lazik,* Doris Vetterlein, Simone Kilian Salas, Pramit Sood, Bernd Apelt, and Hans-Jörg Vogel

Biological activity in soil causes fluxes of O₂ into and CO₂ out of the soil with significant global relevance. Hence, the dynamics of CO₂ concentrations in soil can be used as an indicator for biological activity. However, there is an enormous spatial and temporal variability in soil respiration, which has led to the notion of hotspots and hot moments. This variability is attributed to the spatiotemporal heterogeneity of both plant–soil–microbiome interactions and the local conditions governing gas transport. For the characterization of a given soil, the local heterogeneities should be replaced by some meaningful average. To this end, we introduce a line sensor based on tubular gas-selective membranes that is applicable at the field scale for a wide range in water content. It provides the average CO₂ concentration of the ambient soil along its length. The new technique corrects for fluctuating external conditions (i.e., temperature and air pressure) and the impact of water vapor without any further calibration. The new line sensor was tested in a laboratory mesocosm experiment where CO₂ concentrations were monitored at two depths during the growth of barley (Hordeum vulgare L.). The results could be consistently related to plant development, plant density, and changing conditions for gas diffusion toward the soil surface. The comparison with an independent CO₂ sensor confirmed that the new sensor is actually capable of determining meaningful average CO₂ concentrations in a natural soil for long time periods.

Abbreviations: ET, evapotranspiration; IR, infrared.

Abiotic and biotic parameters determine C turnover and soil respiration at different spatial and temporal scales ranging from small soil aggregates to landscape scale and from fast to very slow processes (Reichstein and Beer, 2008; Stoyan et al., 2000; Bekele et al., 2007). Soil respiration depends on inputs of easily available C sources via plants, the presence of roots, microbes, and fauna, as well as abiotic conditions (temperature, pH, water and nutrient availability).

Soil respiration is frequently investigated based on indirect CO₂ efflux measurements at the soil surface (Rochette and Hutchinson, 2005). The CO₂ efflux measured at the surface can be correlated with these abiotic parameters and biotic influencing factors (Reichstein and Beer, 2008). A direct link between CO₂ efflux and soil respiration presumes that the transport processes are in a steady state and no additional CO₂ sinks and sources are present (Cerling, 1984; Amundson et al., 1998; Amundson, 2001). However, soil respiration and gas transport can be highly variable, and as a consequence steady state may not be reached (Koehler et al., 2010; Maier et al., 2010, 2011). In addition, based on weekly measurements, Risk et al. (2002) showed for various sites that the CO₂ flux measurements at the soil surface do not necessarily reflect the CO₂ production in the soil. They attributed this to the dominant influence of the upper soil layer (some centimeters) on the CO₂ efflux, which may mask the dynamics of CO₂ production of the root zone.

It is well known that different soil types differ in terms of biological activity and C turnover. Hence, given a specific soil type, we are interested in a mechanistic understanding of gas exchange processes and soil respiration for this soil at the pedon or field scale. The aim is to characterize this soil in terms of soil–plant–microbe interaction, greenhouse gas production, and the soil gas dynamics, which are important factors affecting soil fertility.
and plant growth (Ben-Noah and Friedman, 2018). Compared with basic soil properties (e.g., soil texture, porosity), direct information on O₂ and/or CO₂ concentrations has been determined to be more sensitive for the evaluation of soil aeration and respiration (Klimanek and Greilick, 1981; Ben-Noah and Friedman, 2018).

Direct measurements of soil gas concentrations can thus be highly valuable to improve our mechanistic understanding of biological soil processes and their interaction with physical soil properties (Suarez and Šimůnek, 1993; Šimůnek and Suarez, 1993; Risk et al., 2002; Hashimoto and Komatsu, 2006; Taneva et al., 2006; Riveros-Iregui et al., 2007; Blagodatsky and Smith, 2012; Wiaux et al., 2015). Direct measurements of CO₂ concentrations, together with modeled or estimated diffusivity, provide direct information on depth-dependent respiration and flux as implemented in the soil-CO₂ profile method (Risk et al., 2002; Hirano et al., 2003; Pumpenan et al., 2003a; Tang et al., 2003; DeSutter et al., 2008; Han et al., 2014; Xiao et al., 2015; Wiaux et al., 2015). With these targets, we worked on a sensor to measure CO₂ concentration for a larger, more representative soil volume.

Various technologies are still available to measure the concentration of soil gases, especially of CO₂. These technologies include manual sampling techniques, sampling traps and diffusion probes, and in situ sensing technologies. They all have specific potentials and limitations:

### Soil Gas Measurement

#### Manual Sampling

To extract soil gas from different depths, pumps and syringes are used (Kerfoot et al., 1988; Wood et al., 1993; Koehler et al., 2010). The gas samples are analyzed with various standard analytical techniques ranging from simple infrared (IR) CO₂ gas sensors, to laser absorption and modulation spectroscopy, up to gas chromatographs and mass spectrometers. Such techniques enable the analysis of various gas components but are too expensive and laborious for large-scale applications or long-term monitoring. In addition, manual sampling disturbs the surrounding soil and may cause artificial gas fluxes within the sampling region depending on water saturation and soil structural properties.

#### Sampling Traps and Diffusion Probes

Gas sampling traps (Fang and Moncrieff, 1998) and diffusion probes (Kammann et al., 2001; Bekele et al., 2007), with minimum disturbance during sampling, are alternatives to manual sampling. For the separation of soil gas and soil water, nonporous gas-permeable membranes are used (e.g., Jacinthe and Groffman, 2001; Kammann et al., 2001; Panikov et al., 2007; Seethaphathy and Górecki, 2010, 2011, 2012) as well as microporous hydrophobic membranes (Gut et al., 1998; DeSutter et al., 2006; Flechard et al., 2007; Schloemer et al., 2013; Jochheim et al., 2018). Crucial for nonporous probes is the time needed to reach the required partition equilibrium of the gas components between the opposite faces of the membranes. This depends on the membrane size and geometry, its permeability coefficients for gas components, and the volume of gas within the probe. Kammann et al. (2001) determined an equilibration time of 7 h for a silicon tube with an inner diameter of 10 mm, a wall thickness of 3 mm, and an inner gas volume of 100 mL. To enable measurements with higher temporal resolution, highly permeable hydrophobic microporous polypropylene membranes (ACCUREL) were used (Flechard et al., 2007; Schloemer et al., 2013; Jochheim et al., 2018). However, in this case, the outer gas composition can be disturbed due to fast gas exchange, and related dampening effects of the measurement signal need to be considered and minimized (Flechard et al., 2007). Therefore, site-specific adaptation and in situ calibration might be necessary. In long-term applications, (bio)clogging of pores within the membrane can increase the time required for equilibration.

#### In Situ Sensing

Infrared gas sensors encapsulated within a gas-permeable membrane are typically used for local in situ measurement of soil CO₂. They are installed from the soil surface (Tang et al., 2003), from trenches or observation facilities (Hirano et al., 2003; Xiao et al., 2015). The advantage of a permanent sensor installation in the subsurface, which enables highly resolved gas monitoring, competes with the disadvantage that calibration and maintenance is problematic within the soil. Increasing uncertainties with time, e.g., due to the drift in sensor characteristics, require periodic dismounting and maintenance of the sensors. In contrast to the local scale of gas analysis with such in situ sensing, the scale for surface-based measurements, e.g., with respect to the measurement of CO₂ effluxes, is much larger and defined by the surface area of flux chambers or by the footprint of eddy covariance towers. However, flux chambers at the soil surface are still relatively small with respect to the spatial structure of hotspots in biological activity, so that the results are typically afflicted with considerable variance (Jensen et al., 1996; Stoyan et al., 2000).

Based on selective diffusion through tubular gas-selective membranes, a new sensory principle was introduced for the measurement of CO₂ or O₂ concentrations (Lazik and Geistlinger, 2005; Lazik et al., 2009; Lazik and Sood, 2016). The tubular sensor (called a line sensor) provides an arithmetic average of fluctuating CO₂ concentrations along its length. This sensor has the potential to close a gap of in situ sensing: it combines large spatial coverage (possible length of some decimeters to a few tens of meters) with high temporal resolution (minutes).

The initial development of the line sensor was motivated by the need to detect and quantify CO₂ leakages from subsurface gas repositories (Lazik and Ebert, 2013; Neumann et al., 2016a, 2016b; Lazik et al., 2016) where higher concentrations are expected compared with uninfluenced soils. For this application, the gas-selective membrane of a line sensor was combined with a gas-tight reference membrane to compensate for environmental parameters (air pressure, soil temperature). For measuring soil respiration, this technique needs to be sensitive for very low CO₂ concentrations.
Besides the impact of soil temperature and air pressure, also that of water vapor pressure needs to be considered.

This study used a new type of line sensor for the measurement of low CO₂ concentrations in aerated humid soil. It demonstrates how the measurement signal for CO₂, which is based on pressure changes, can be discriminated from that of water vapor, although the vapor-related pressure change is one order of magnitude higher and shows temporal dynamics similar to that of CO₂. The performance of the new sensor type was demonstrated in a mesocosm experiment in which soil respiration was promoted by plants. An unplanted control served as comparison, providing basal soil respiration related to mineralization of soil organic matter.

Line Sensors for Aerated Humid Soils

Basics

The measurement principle is based on the change in the number of gas molecules within a tube (the measurement chamber) caused by selective diffusion of different gas components through its wall—a nonporous symmetric membrane. The measurement chamber and the gas-selective membrane form the measurement cell (called the gas-selective cell) of such a sensor. Initially purging the measurement chamber with a gas of known composition is required to establish steady-state diffusive fluxes within the membrane (conditioning step). If the measurement chamber is then closed at time \( t = t_0 \) (measurement step), the change in the number of gas molecules can be measured as a pressure change according to the ideal gas law and Dalton’s law of partial pressure. Near the humified soil, temperature-dependent changes in the water vapor concentration need to be considered. To allow for measurable pressure changes, the water-vapor-saturated stratum is expected to contain the mole fractions \( x^\text{i.s.} \) (superscript i.s. denotes the internal gas standard, subscript \( x \) = CO₂). This is known and therefore forms an internal standard for a permanent in situ calibration as introduced by Lazik and Sood (2016):

\[
\Delta p^\text{ex} = \alpha - \varepsilon (\Delta p^\text{ex}) + p^\text{ex}^\in \varepsilon \approx gP_s \left( p^\text{ex} - p^\text{in} \right) \sum_j \chi_j^\text{ex} \chi_j^\text{in}
\]

The offset \( \varepsilon \) depends on the measurement conditions, i.e., the pressure difference between the purge gas pressure within the measurement chambers \( p^\text{in} \) and the air pressure \( p^\text{ex} \) outside the sensor and the purge gas composition \( \chi^\text{in} \). It can be determined theoretically and experimentally.

Up to now, the pressure change was measured against a gas-tight reference measurement cell (called the reference cell) to account for the impact of environmental parameters (temperature, air pressure). Both measurement cells were purged and closed simultaneously during the conditioning step and the measurement step, respectively. For detecting small CO₂ concentrations in a humid soil, temperature-dependent changes in the water vapor pressure have to be taken into account as an additional effect. To this end, the gas-tight reference cell was modified. The new reference cell (Fig. 1) is constructed the same as the gas-selective cell but its outer membrane surface is covered by water-vapor-saturated air kept in place by a gas-tight coating. This water-vapor-saturated stratum is expected to contain the mole fractions \( x^\text{hr} \) (superscript hr for humid reference). It is exposed to the same environmental conditions prevalent in the ambient soil.

For small times \( \delta t \) of a measurement step, the pressure difference \( \Delta p \) in Fig. 1 is \( p^\text{in} - p^\text{hr} \). According to Eq. [1], the pressure change \( \alpha \) depends on the differences in the outer partial pressures \( p^\text{ex}(x^\text{ex} - x^\text{hr}) \). Hence, the pressure change will be independent of the composition of the purge gas within the measurement chambers. Due to the same environmental conditions within the soil and the water-vapor-saturated stratum (the humid reference), this independence causes the elimination of pressure effects related to water vapor. Thus, the theoretical framework developed by Lazik and Sood (2016) is still valid and enables CO₂ measurement without further calibration as described above.

Line Sensor Prototypes

We constructed 12 line sensors, each consisting of two gas-selective cells and a reference cell using PDMS tubing (Versilic
SPX-50 tubing, Saint Gobain Performance Plastics) as gas-selective membranes. The tubes \((2R_i = 1/32 \text{ inches} \approx 0.8 \text{ mm}, 2R_o = 3/32 \text{ inches} \approx 2.4 \text{ mm})\) were cut into pieces of 2.5-m length. The tubes for the reference cells were covered in cotton hoses and then mantled by polyurethane tubing \((2R_i = 5 \text{ mm}, 2R_o = 6 \text{ mm})\). The cotton hoses were moistened to generate a water-vapor-saturated environment around the reference membranes. Moisture losses during the experiment were compensated by a feed of distilled water over the tube connected to a storage vessel.

The permeability coefficients of the polydimethylsiloxane material are in general not provided by manufacturers. It may actually vary depending on the production process, and information from the existing literature is limited. Merkel et al. (2000) gave the following values \(\{\text{CO}_2, \text{O}_2, \text{N}_2\} = \{38, 8, 4\} \times 10^{-8} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s cm Hg})\), but the permeability for water vapor was not determined. Robb (1968) specified the permeability coefficient of water vapor in a polydimethylsiloxane membrane containing 30% filler to \(360 \times 10^{-8} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s cm Hg})\). To estimate a permeability coefficient for water compatible with the more recent study by Merkel et al. (2000), we used the ratio of the permeability coefficients for CO\(_2\) from both works as a scaling factor and obtained \(420 \times 10^{-8} \text{ cm}^3 \text{ cm}/(\text{cm}^2 \text{ s cm Hg})\).

To control the cyclic measurement of conditioning and measurement steps (see above), actuator units (black cases in Fig. 2) were designed containing a processor for analyzing and transmitting the pressure changes. For pressure measurement, we used AMS 5812-0000-D-B pressure sensors (pressure range \(\pm 0.517 \text{ kPa}, \text{Amsys}\)). To open and close the ends of a line sensor, a pinch valve \((108P8NO12–01B, \text{Bio-Chem Fluidics})\) was used. One gas-selective cell per line sensor and the reference cell were purged by dry air from a compressor. The purge gas for the other gas-selective cell was mixed from compressor air and CO\(_2\) and adjusted to a CO\(_2\) mole fraction of 1.5%. The time span for the conditioning step was set to 55 s and that for the measurement step to 5 s. The conditioning step caused the formation of a pressure gradient within the tubular measurement chambers, which equilibrates after closing the measurement chambers at the start of measurement. To minimize the influence of this relaxation process on the measurement signal, an offset time of 0.5 s was chosen between the closing of the measurement chambers and the start of the pressure registration. The individual sensor units were integrated in a serial RS-485 bus. A bus master module was developed to sequentially retrieve the analyzed data from the actuator units (resolution at each measurement point: 132 s). From this, the data were transmitted to

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Fig. 2. Experimental setup (left): Mesocosms B-1 to B-6 with air-dried soil during initial watering. The actuator units for CO\(_2\) measurement (black cases at the front side) are connected to the line sensor tubes as shown on the right. Each line sensor consists of two white-colored tubes (gas-selective cells 1 and 2) and a red tube (reference cell).
a laptop together with time stamps and the air pressure (measured with the bus master module with the separate pressure sensor AMS 5812–0150-B, Amsys).

The purge gas pressures were defined using glass tubes that were immersed about 15 cm into a water bath. The purge gas flows were adjusted by mass flow controllers (MFC 8710, ranges: 0–0.25 L min⁻¹ for CO₂ and 0–5 L min⁻¹ for air; Bürkert Fluid Control Systems). The CO₂ mole fractions of the purge gases were analyzed with calibrated IR CO₂ sensors (GMP-221, mole fraction range 0–5%, Vaisala).

**Experimental Investigation**

**Mesocosms**

Six mesocosms (50 by 50 cm, height 55 cm) were prepared from 12-mm polyvinyl chloride plates (Fig. 2). Polyvinyl chloride collars were placed at the upper edge. Three sides per mesocosm were thermally insulated with 2-cm polyurethane insulation sheets; the front sides that were used for installation of measurement gauges remained without insulation. The base plates were uniformly perforated with 25 boreholes of 30-mm diameter. The boreholes were covered by 30-μm mesh to enable water movement while preventing the loss of soil and roots. The mesocosms were placed on 6-mm spacers in stainless steel tanks. Plant lamps (MGR 400 with SON-TP Agro 400 W lamp, 55 × 10³ cd sr, Philips) were installed from the ceiling with a vertical distance of 60 cm to the collars of the mesocosms.

Water losses through evapotranspiration were replaced from the bottom via water-level controlled peristaltic pumps. The pumps were adjusted to a fixed flow rate and were switched on or off depending on a minimum and maximum water level. The added water was calculated from the running periods of the pumps.

Line sensors were installed during filling of the mesocosms with soil (Fig. 2, detailed below) at two observation depths of 5 and 15 cm below the soil surface. The length (2.5 m) and arrangement of the line sensors (Fig. 2) was chosen to enable a representative measurement of CO₂ for the respective depth. For measuring matric potential, water content, and temperature, a miniature tensiometer (T5, Umweltanalytische Mess-Systeme), a time-domain reflectometry sensor (Institute of Agrophysics, Polish Academy of Sciences), and a temperature sensor (Pt100, Omega Engineering) were installed at each observation depth. In addition, four temperature sensors (Pt100) were installed 5 cm above the soil surfaces on the collars. Tensiometers as well as time-domain reflectometry sensors were calibrated in a homogeneous soil, the factory-calibrated sensors, tests were performed during the preparatory phase for different purge gas pressures and various concentrations of the internal standard. On 9 Aug. 2016, the illumination by plant lamps started. The mesocosms were illuminated for 12 h d⁻¹ from 08:00 to 20:00. As expected, plant lamps induced fluctuations of temperature, in particular at the soil surface. On 18 Oct. 2016, the soil surfaces of all mesocosms were covered with bits of polystyrene to reduce soil heating and evaporation of water. On 23 Oct. 2016, the soil-filled mesocosms were considered to be sufficiently stabilized (no more significant soil settlement, stabilization of C turnover after initial watering).

**Experimental Protocol**

The mesocosm experiment was divided into three phases: a preparatory phase, the actual plant growth phase, and a final phase to compare the line sensor measurements with an independent measurement technique. Table 1 summarizes the schedule.

<table>
<thead>
<tr>
<th>Table 1. Action summary (the start of Phase 2 is referred to as Day 0).</th>
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<tbody>
<tr>
<td>Time</td>
</tr>
<tr>
<td>13 June 2016</td>
</tr>
<tr>
<td>20 June 2016</td>
</tr>
<tr>
<td>9 Aug. 2016</td>
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<tr>
<td>18 Oct. 2016</td>
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<tr>
<td>19 Nov. 2016</td>
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<tr>
<td>12 Dec. 2016</td>
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<tr>
<td>13 Jan. 2017</td>
</tr>
<tr>
<td>16 Jan. 2017</td>
</tr>
<tr>
<td>18 Jan. 2017</td>
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<tr>
<td>23 Jan. 2017</td>
</tr>
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</table>

**Phase 1: Preparatory Phase**

The mesocosms were filled with soil from an agricultural field test site in Bad Lauchstädt (Chernozem, 0–10-cm depth) described by Altermann et al. (2005). The soil had an organic C content of 2.1%; the carbonate content was below the detection limit (<0.1%). The soil was homogenized, sieved to 2 mm, air dried, and stored at room temperature until setup of the experiment. The mesocosms were uniformly filled and consolidated layerwise up to a height of 50 cm. On 13 June 2016, the continuous watering started from the bottom with distilled water. The water table was adjusted to a depth of 44 cm from the soil surface. After about 2 wk, steady-state saturation profiles were reached for all mesocosms. On 20 June 2016, the line sensor network was activated for measurement of CO₂ concentrations at the 5- and 15-cm depths. To check the response behavior of the line sensors, tests were performed during the preparatory phase for different purge gas pressures and various concentrations of the internal standard. On 9 Aug. 2016, the illumination by plant lamps started. The mesocosms were illuminated for 12 h d⁻¹ from 08:00 to 20:00. As expected, plant lamps induced fluctuations of temperature, in particular at the soil surface. On 18 Oct. 2016, the soil surfaces of all mesocosms were covered with bits of polystyrene to reduce soil heating and evaporation of water. On 23 Oct. 2016, the soil-filled mesocosms were considered to be sufficiently stabilized (no more significant soil settlement, stabilization of C turnover after initial watering).
Phase 2: Plant Experiment

On 24 Oct. 2016 (referred as Day 0 here), the polystyrene was removed from the randomly selected mesocosms B-4 to B-6 (nomenclature in Fig. 2). One hundred seeds of barley, soaked in CaSO₄ for 2 h prior to seeding, were sown per mesocosm. The mesocosms B-1 to B-3 were operated as unplanted controls. On 28 Oct., 1 Nov., 4 Nov., and 7 Nov. 2016, the soil surfaces of all mesocosms were additionally irrigated manually from the top to enable homogeneous germination of the seeds. Occasional weed plants were removed. On 12 Dec. 2016, the barley was harvested and dried at 60°C for determining shoot dry weight. The experiment was continued after harvest.

Phase 3: Comparison of Line Sensors and Infrared Carbon Dioxide Sensor

A comparison of line sensor measurements with CO₂ measurements at the surface was performed after harvest on bare soil. To this end, the mesocosms were covered with gas-tight foil on 13 Jan. 2017. The foil was fixed on the collars with tape and loaded with sand to prevent blowing up. To adjust different CO₂ concentrations, small flows of CO₂–air mixtures were directed to the covered soil surfaces using a tubular network. The surface concentration was measured on one of the mesocosms (B-4) using an IR CO₂ sensor (GMP221, measurement range 0–10%, Vaisala), which touched the soil directly. The CO₂ concentrations at the soil surfaces of the mesocosms had to equilibrate to compare the surface measurement values from Mesocosm B-4 with the line sensor measurements. Dilution effects on the CO₂ concentration caused by leaks (between the covering foil and the edges of the mesocosms and through boreholes at the front sides of the mesocosms) were compensated by a continuous inflow of the CO₂–air mixture. To avoid an increase in pressure, we started with a small flow rate and increased it in steps. Details are given in Table 1.

On 26 Jan. 2017, the settlement heights of the soil were measured and the soil was extracted in layers. Undisturbed soil samples were taken from various depth ranges (Table 2). For root length density determination, two soil samples (volume: 166 cm³) from each depth range were extracted, and roots were separated from the soil by washing with distilled water using a sieve with a mesh size of 1 mm. Root length was determined with the WinRhizo system (WinRhizo Pro 2009b, Regent Instruments). Bulk density (ρₚ) was obtained from two further sets of undisturbed soil samples with volumes of 100 cm³ (three samples per mesocosm in the depth ranges 0–4, 5–9, and 15–19 cm), and 250 cm³ (two samples per mesocosm at 5–10 and 15–20 cm) after drying for 24 h at 105°C. Soil porosity φ = 1 − ρₖ/ρₚ was determined from the bulk density and a particle density of ρₚ = 2.63 g cm⁻³, which was averaged from measured values of previous studies (Altermann et al., 2005; Franko et al., 2007).

Data Preparation

The measurements obtained from the different measurement systems were stored in various formats with different temporal resolutions. In addition, the pressure change measurements were time-shifted depending on the logical position of the respective actuator within the serial bus. Automated data processing was implemented using Mathematica 11 (Wolfram Research).

The measured values (air pressure, temperatures, CO₂ concentrations of purge gases, etc.) used for calculating the soil CO₂ concentration were synchronized in time with the readings of the pressure changes α and α’ in Eq. [2]. All experimental data including the calculated soil CO₂ concentrations were transformed to a consistent dataset with uniform reference times and a temporal resolution of 10 min. Data with a higher temporal resolution were smoothed accordingly.

Outliers were removed from the data sets by simple plausibility tests and statistical tests. The plausibility of the respective data was ensured by visual identification and the definition of plausibility thresholds. With regard to the application of statistical outlier tests, it was necessary to consider the fact that the measured values may show sudden changes (edges). Such edges resulted, e.g., from rapid changes in air pressure, the opening of a door, or the switching on or switching off of lighting or the air conditioning system. In these cases, automatic outlier detection, preferably by comparing the measured values with a moving average, is problematic. Therefore, a bilateral filter (Tomasi and Manduchi, 1998) from image processing was used. This is a nonlinear local filter for edge-preserving smoothing implemented in Mathematica 11. The filter was adapted so that edges were displayed visually correct. The mean deviation between measured and filtered data was interpreted as a standard deviation. Measured values were identified as outliers and removed if their difference from the filtered data exceeded four times this standard deviation (corresponding to a confidence interval of 99.994%).

The soil CO₂ concentrations were calculated from the recorded pressure changes α and α’ as discussed above using the known compositions and pressures of the purge gases (details above and Fig. 3) as required by Eq. [2]. The IR CO₂ sensor records were corrected with regard to environmental parameters (air pressure, room temperature) according to the guidelines of the manufacturer (available online). The air-filled porosity θₕ (cm³ gas)/(cm³ soil) was calculated from the porosity, and the soil

<table>
<thead>
<tr>
<th>Mesocosm</th>
<th>s (cm)</th>
<th>ρₚ (g cm⁻³)</th>
<th>σ (%)</th>
<th>u (%)</th>
<th>n (samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1, B-2, B-3 (unplanted)</td>
<td>(1.3 ± 0.5)–4</td>
<td>1.02</td>
<td>0.11</td>
<td>10.3</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>5–10</td>
<td>1.26</td>
<td>0.04</td>
<td>3.3</td>
<td>14</td>
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<tr>
<td></td>
<td>15–20</td>
<td>1.27</td>
<td>0.04</td>
<td>2.8</td>
<td>15</td>
</tr>
<tr>
<td>B-4, B-5, B-6 (planted)</td>
<td>(1.3 ± 0.3)–4</td>
<td>0.98</td>
<td>0.04</td>
<td>4.6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>5–10</td>
<td>1.22</td>
<td>0.03</td>
<td>2.4</td>
<td>15</td>
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<tr>
<td></td>
<td>15–20</td>
<td>1.24</td>
<td>0.03</td>
<td>2.0</td>
<td>15</td>
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</table>
water saturation was obtained from the time-domain reflectometry sensors. The evapotranspiration (ET) was estimated based on the consumption of water for irrigation supplied from the bottom by the pumps and the additional manual irrigation from the top.

Results and Discussion

Environmental Conditions

Figure 3 shows the environmental conditions during Phases 2 and 3 of the experiment. The air temperature (mean values from two sensors each) measured 5 cm above the soil surface of the mesocosms showed significant differences. With increasing shading by the plant canopy, the average air temperature decreased and the daily dynamics became comparatively smaller. The decreasing amplitude of the air temperature above unplanted mesocosms toward the end of Phase 2 was probably caused by shadowing effects from neighboring planted mesocosms. Because the mesocosms were covered with foil during Phase 3, their daily illumination led to an increase in mean air temperature and its amplitude.

In addition to the concentration (mole fraction) of CO$_2$ in the room air, $c_{CO2}$, Fig. 3 shows the air pressure $p_{air}$. Both variables are involved in the determination of soil CO$_2$ concentrations according to Eq. [2].

Plant Development

One week after seeding (Day 7, Fig. 3) the plant development reached the two-leaf stage in all mesocosms and a closed canopy after 4 wk (Day 28). However, the plant density showed high variability among the three replicates (Fig. 4a). A possible explanation could be different intensities of additional illumination by daylight. However, this was not detrimental for our experimental approach because differences in plant growth and density should be reflected in different CO$_2$ concentrations in the rhizosphere.

Root length density (Fig. 4b) was determined at the end of the experiment because destructive sampling was required. The two samples from each depth were positioned randomly and bulked after washing because they were supposed to provide a representative result for their respective depths. The near-surface root length density as well as its depth gradient correlated well
to the plant density–shoot dry weights after harvest: 254 g (B-4), 180 g (B-5), and 139 g (B-6). The low value obtained for B-6 in the 0- to 5-cm depth followed by a high value for the same mesocosm in the 5- to 10-cm depth is a result of the discretionary selected depth increments for destructive sampling and did not change the general picture.

**Soil Parameters**

The bulk densities (Table 2) of the unplanted soils were slightly higher than that of the planted soils and showed a higher variability. For the field site from which the soil for our plant experiment was taken, bulk densities of 1.33 g cm\(^{-3}\) for the 0- to 10-cm depth and 1.26 g cm\(^{-3}\) for the 10- to 20-cm depth were reported for field structured soil (Franko et al., 2007). With the exception of the very low bulk densities in the upper 5 cm of mesocosms, settling of the soil (about 1.3 cm, Table 2) resulted in bulk densities that correspond to 1.26 g cm\(^{-3}\), which was measured in the 10- to 20-cm soil layer at the field site. However, the sieved, dried, and homogenized soil used in the mesocosms did not reach the bulk density of 1.33 g cm\(^{-3}\) described for the original soil layer in 0 to 10 cm (see above).

Soil porosities (Fig. 5) were determined from the bulk densities of the individual soil samples (\(\eta\) in Table 2). Both the unplanted as well as planted soils show the highest porosities in the upper 5 cm. While B-1 has a comparatively narrow porosity–depth distribution, this is comparatively wide in the case of B-3. Among the unplanted mesocosms, the variability and depth distribution of porosity of B-2 were most similar to the planted mesocosms. Therefore, we focus in the following on B-2, as a representative for an unplanted treatment, and compare this to the planted treatments B-4 to B-6. Appendix A shows the variability in CO\(_2\) concentrations among the unplanted treatments.

**Line Sensor Based Measurements of Carbon Dioxide**

**Comparison of Line Sensors and Infrared Carbon Dioxide Sensor**

The two surface concentrations of 1.47 and 2.38% CO\(_2\) imposed on Days 81 and 86, respectively, were quickly reached (Fig. 6), while the line sensors approached these values only gradually, starting from initial CO\(_2\) concentrations in the soils, which were different for the various mesocosms.

Remarkably, all line sensors matched the surface concentration almost perfectly. It has to be emphasized that these results were obtained without any additional calibration of the line sensors after about half a year of continuous operation time.

From this good match we conclude that the complete line sensor surface contributed to the measurement. This also indicates that the soil CO\(_2\) concentration around a line sensor had reached partition equilibrium between the phases of soil air and pore water (inclusive of the water films on aggregates or roots that touch the line sensors). In reverse, this demonstrates that the line sensor provides a meaningful average that is independent of the phase composition.

The remaining differences of about 5% of mole fraction could be explained by dilution effects due to leaks between the foil and the walls of the mesocosms. This could result in lower CO\(_2\) concentrations at the surface and, hence, also lower concentrations in the soil. As described under Experimental Observations, the CO\(_2\) concentrations at the soil surface were measured only in Mesocosm B-4. However, the measurements in the soil of the other mesocosms indicate a similar situation.

Also, locally incomplete phase equilibrations would result in a reduced mean soil CO\(_2\) concentration. In addition, the measurement uncertainty and bias of the sensors, which was investigated under precisely defined dry-gas conditions by Lazik and Sood (2016), will have contributed to this 5% difference.

**Compensation for Water Vapor**

As described above, the permeability coefficient of water vapor of the gas-selective membrane is one order of magnitude higher than that of CO\(_2\). In addition, the mole fraction of water vapor (\(X_{H_2O}\)) exceeded that of CO\(_2\) (\(X_{CO_2}\)) in the plant experiments, as shown for Mesocosm B-4 (15-cm depth) in Fig. 7c and 7d. For the measured soil temperature range (Fig. 7e and 7f) from 18 to 24°C, the mole fraction \(X_{H_2O}\) (black in Fig. 7c and 7d) calculated with the Magnus formula ranged between 2 and 3%. However, \(X_{CO_2}\)
(red in Fig. 7c and 7d) reached a maximum level of only about 2.3\% during plant growth. In addition, the dynamics of both $\chi_{\text{CO}_2}$ and $\chi_{\text{H}_2\text{O}}$ (Fig. 7d) are correlated with the diurnal dynamics of soil temperature (Fig. 7f). That means the diurnal dynamics of $\chi_{\text{CO}_2}$ and $\chi_{\text{H}_2\text{O}}$ are similar to each other.

To illustrate the different impacts of water vapor pressure on the measurement, we compared the current measurement signal (red in Fig. 7a and 7b) with that of an equivalent line sensor with a gas-tight reference. We assumed the same measurement conditions for both line sensor types. To calculate the pressure change caused by water vapor (Fig. 7c and 7d), the sensor slope for detection of $\chi_{\text{H}_2\text{O}}$ was determined based on the known sensor slope for $\text{CO}_2$ and the ratio of permeability coefficients of the membrane for water vapor and $\text{CO}_2$ (see above). Based on this, the theoretically
expected pressure change for the water vapor pressure (black in Fig. 7a and 7b) and the total pressure change (green in Fig. 7a and 7b) were calculated—the latter considers the additivity of the pressure changes (see above) for water vapor and the actual measured pressure change for CO$_2$. This total pressure change, which differs only a little from the pressure change for water vapor, would be detected using a line sensor with a gas-tight reference.

In contrast, the membrane of the introduced new reference type is embedded in a water-vapor-saturated atmosphere. Thus, the water vapor fluxes into the measurement chamber are balanced by that into the reference chamber. Therefore, the dominant influence of water vapor on the measurement signal is compensated (shift from green to red curve in Fig. 7a and 7b), and the line sensor provides highly resolved measurement data on CO$_2$ dynamics (Fig. 7b and 7d).

**Carbon Dioxide Dynamics in Soil**

The dynamic of CO$_2$ concentrations during plant growth is shown in Fig. 8 for two different depths together with the dynamics of gas-filled porosity ($\theta_g$), matric potential ($\psi_m$), and evapotranspiration (ET). The unplanted reference is shown on the left, followed by the planted mesocosms with increasing plant and root densities. The tensiometers installed in B-6 and B-4 at the 5-cm depth failed during the experiment, leading to incomplete datasets. Steep declines in $\theta_g$ and $\psi_m$ during the first days are related to irrigation events from the top (indicated by orange lines).

During plant growth, CO$_2$ concentrations were highly correlated with plant densities, while harvesting at Day 49 (indicated by dashed black arrows) caused a sharp drop in concentrations in all planted mesocosms.

![Fig. 8. Dynamics of CO$_2$ concentration ($\chi$), air filled porosity ($\theta_g$), and matric potential ($\psi_m$) for the observation planes at 5-cm (black) and 15-cm (blue) depths as well as evapotranspiration (ET) for the unplanted reference followed by the planted mesocosms. Orange markers indicate additional surface irrigation, red arrows show the CO$_2$ maxima, and black arrows indicate the date of harvesting. The red dashed line indicates the matric potential that causes wide macropores (>50 $\mu$m) to drain.](image-url)
Evapotranspiration measured in the unplanted control can be taken as a measure for evaporation for both treatments. Evapotranspiration in the planted treatments, which is clearly dominated by transpiration, increased with plant development and is correlated with the planting density and biomass. However, in contrast to ET, the maximum CO₂ concentrations were already reached several days before harvest. Indicated by dashed red arrows, this peak was reached first for the highest plant density (B-4, Day 30) and last for the lowest density (B-6, Day 35), while ET was still increasing in all mesocosms until harvest. Hence, the CO₂ concentrations were declining while the plants were still growing with their stomata open. In the unplanted control, a gradual increase in concentration was observed in the 15-cm depth but no change in ET.

The early decrease in CO₂ concentration before the maximum transpiration might be the result of increased gas diffusion toward the soil surface caused by decreasing water content in the upper soil layer of the planted treatments. The unplanted mesocosm shows the lowest θg levels without much variation, especially in the second depth, but small values of matric potential that are comparable to the initial matric potentials of the planted treatments (up to Day 30). Hence, the proportion of macropores seems to be reduced due to a comparatively stronger compaction. This lower air-filled macroporosity hampers gas flux, which may explain the gradually increase of CO₂ concentration in the 15-cm depth.

Especially for the highest plant density (B-4), a gradual increase of air-filled porosity was observed close to the time for maximum concentrations that continued up to harvest. Obviously, plant water extraction in the 5- and 15-cm depths was quicker than water movement from the water table at the 44-cm depth to this layer. Hence, the water potential gradient between soil layers increased with time and increasing plant size. As a result, soil matric potential decreased in these layers, so that larger pores (>50 μm with a corresponding matric potential of about −60 hPa as indicated in Fig. 8) became air filled. Consequently, the improved gas transport toward the surface led to a drop in CO₂ concentration. This interpretation is corroborated by the observation that the maximum in CO₂ concentrations corresponds to this critical matric potential of about −60 hPa in all mesocosms (red dashed lines). During decreasing CO₂ concentrations (after Day 30), smaller pores (10–50 μm at ψm < −300 hPa) were also drained at the 5-cm depth and partly at the 15-cm depth. Hence, the observed CO₂ peak indicates the moment where CO₂ flux toward the soil surface overtakes the accumulation of CO₂ from soil respiration. This demonstrates the importance of transient gas transport for the interpretation of the measurements toward soil respiration as stated, e.g., by Maier et al. (2010, 2011).

Due to the temperature dependency of CO₂ production and evapotranspiration, the diurnal CO₂ fluctuation is correlated with soil temperature as shown in detail in Fig. 7. These fluctuations were small compared to the total magnitude of CO₂ from soil respiration shown in Fig. 8.

The large supporting volume of the measurement allows averaging across small-scale heterogeneities as well as across spatiotemporally changing hotspots and hot moments of root respiration (Kuziyakov and Blagodatskaya, 2015). This may facilitate the joint evaluation of CO₂ production and transport and improve our quantitative process understanding for the field scale based on mechanistic modeling.

We measured CO₂ concentrations of up to 2.4% in our mesocosms. Klimanek and Greilick (1981) found CO₂ concentrations in soil air of up to 2.9% in field experiments while examining the influence of bulk density on soil aeration for the same soil (a Chernozem at Bad Lauchstädt). A large number of field studies and field experiments have reported similar concentration ranges with maxima in the range of 1 to 5% (e.g., Pumpanen et al., 2003a, 2003b; Doff Sotta et al., 2004; Riveros-Iregui et al., 2007; DeSutter et al., 2008; Koehler et al., 2010; Ek and Godissart, 2014; Han et al., 2014; Roland et al., 2015; Fan et al., 2016). Others have observed soil respiration processes at CO₂ concentrations below 1% (Risk et al., 2002; Jochheim et al., 2018), while concentrations of up to 10% have also been reported (Oh et al., 2005; Taneva et al., 2006; Bekele et al., 2007; Jaakkola and Simojoki, 2008; Wiaux et al., 2015). The line sensor presented here covers the entire range of typical CO₂ concentrations in soil with high precision. This was demonstrated for <1.6% CO₂ by Lazik and Ebert (2012) and for concentrations <8% by Lazik and Sood (2016) for dry gases. In this study, we demonstrated the applicability of the line sensor for natural, humid soil conditions. Thus, we conclude that the actual development of this technique allows a precise monitoring across the possible concentration ranges of CO₂ in soils. This should be further verified in field tests.

**Summary and Conclusion**

We present a new technique to measure the average CO₂ concentration in soil along the length of a tubular sensor. The construction of the new sensor allows correcting for environmental factors such as soil temperature, air pressure, and water vapor without any separate calibration. Due to the large supporting volume of the measurement, this technique provides a meaningful measure of CO₂ for heterogeneous materials such as soils. The average CO₂ concentration considers both the concentrations in soil air and the water phase. With a high temporal resolution in the range of minutes, the new technique has the potential to monitor biological activity in soil.

Soil CO₂ concentration was observed for several weeks in three mesocosms with fast-growing barley and an unplanted control. In an early stage of plant growth, the increasing soil CO₂ concentration was mainly controlled by the increase in soil respiration, i.e., the rise of root respiration and microbial respiration (fueled by root exudation), while CO₂ concentrations increased with plant density. With increasing plant water demand, depending on plant density, soil moisture was reduced so that CO₂ diffusion toward the soil surface was facilitated and CO₂
concentrations were reduced. Monitoring of CO₂ using the new line sensor nicely reflected the interaction between these coupled transient processes.

Although the studied mesocosms were homogeneous in terms of soil structure and plant densities, we are confident that the new technique will provide meaningful average CO₂ concentrations also in heterogeneous environments. This is corroborated by the fact that the sensor characteristic is linear (Lazik et al., 2016). Therefore, the CO₂ concentrations measured consistently reflect the different plant densities. In previous experiments, line sensors with lengths of up to 40 m were successfully tested in soil (Lazik and Ebert, 2013; Neumann et al., 2016b; Lazik et al., 2016). Hence, we conclude that line sensors will have the potential to correctly measure the average CO₂ concentrations in a heterogeneous environment at the field scale, i.e., across several decameters relevant for plant communities.

The results obtained by the new line sensor were successfully confirmed by an independent measurement using an IR sensor. This demonstrated the reliability and robustness of the line sensor even after a half year of continuous operation time. This also demonstrated that this sensor is actually capable of operating in natural soil. Therefore, we conclude that the new sensor type is appropriate to monitor CO₂ concentrations under field conditions over a long time.

Appendix A

The evolution of CO₂ concentrations in the unplanted mesocosms B-1 to B-3 are compared in Fig. A1 for the plant experiment (i.e., Phase 2). The results for the different mesocosms varied in a range of ≈0.3%. Toward the end of the plant experiment, the concentrations tended to converge. The diurnal variations of CO₂ (Fig. A1, right) were very similar, especially in the upper horizon, which suggests similarities in the connectivity of the gas-filled pore networks. Overall, this demonstrates the reproducibility of the results generated by the new sensor.

Author Contributions
Detlef Lazik (DL), Doris Vetterlein (DV), Hans-Jörg Vogel (HJV) developed the test concept. DL and Pramit Sood (PS) developed/validated the new measuring technique theoretically/experimentally. DL, Bernd Apelt (BA), DV, Simone Kilian Salas (SKS) and PS carried out the experimental setup, the monitoring and the final investigations on soil and plants. The results were evaluated by DL supported by BA, DV, HJV and SKS. The manuscript was developed by DL with significant support from HJV and DV.

Conflict of Interest
The authors declare no conflict of interest.

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