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A differential CO2 profile probe approach for field measurements of soil gas diffusivity and soil respiration

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# Abstract

**Background:** Gas exchange between soil and atmosphere is of great importance for greenhouse gas cycles. As gas transport in soil is generally dominated by diffusion the soil gas diffusion coefficient (*D*S) is crucial to understand fluxes between soil and atmosphere. Estimating *D*S is still a great source of uncertainty when calculating soil gas fluxes like soil respiration from soil gas profiles. *In* *situ* measurement of *D*S has the advantage over the application of traditional soil gas diffusivity models that macrostructures and the influence of changing environmental factors can be considered. Even though several methods for *in situ* *D*S measurement exist, they often lack in the temporal resolution to identify short term effects on *D*S or require laborious set-ups which makes them unsuitable for a fast and mobile application.

**Aims:** Our objective was to develop an easy applicable approach to monitor *D*S *in situ* with a high temporal resolution.

**Methods:** We developed a CO2 profile probe with build-in sensors that can easily be installed in soil to gain continuous CO2 concentration profiles. The probe includes the option to inject CO2 as a tracer gas to estimate *D*S. To account for changes in natural CO2 production in the soil we developed a differential approach using two probes, an injection probe and a reference probe. The resulting tracer gas profiles were used to fit a finite element gas diffusion model to derive *D*S. Using the derived *D*S values and the CO2 profiles allowed calculating CO2 fluxes, i.e. soil respiration. The approach was tested with controlled laboratory experiments using different mineral substrates and under natural conditions in the field.

**Results:** The derived *D*S values agreed well with laboratory measurements of *D*S and *D*S-transfer functions. A sufficient tracer signal was required to keep the uncertainty of the *D*S estimation of the topsoil in an acceptable range. Uncertainty in *D*S estimation was lower in the deeper soil due to a stronger tracer signal. The estimated surface CO2 efflux agreed well with chamber measurements. **Conclusions:** This new approach enables monitoring of *D*S and soil respiration *in situ* with high resolution and relatively low effort.

# Introduction

Gas exchange between soil and atmosphere is an important process for soil biology (*Scanlon* et al., 2002) and plays an important role in the global carbon cycle (*Schlesinger* and *Andrews*, 2000). Greenhouse gases such as carbon dioxide (CO2), methane (CH4) and nitrous oxide (N2O) can be produced or consumed in soil depending on soil aeration and biological activity (*Smith* et al., 2018, 2003). Gas transport is therefore an essential mechanism to understand soil processes that affect the greenhouse gas budget of a specific ecosystem.

Gas exchange in soil is generally driven by diffusion. Under special conditions also other processes can influence soil gas transport, e.g. changes in barometric pressure (*Clements* and *Wilkening*, 1974), groundwater level (*Maier* et al., 2010) or wind induced pressure pumping (*Bowling* and *Massman*, 2011; *Laemmel* et al., 2017b; *Maier* et al., 2012). Research showed that such effects can significantly increase gas transport rates and gas flux measurements (*Maier* et al., 2019; *Rey* et al., 2012; *Takle* et al., 2004). For example Laemmel et al. (2019) found that the effective gas diffusivity in a topsoil could be enhanced by up to 30% due to pressure pumping. Still only scarce data about the temporal variability of gas transport rates in soils is available. This makes investigating gas transport in soil with a high temporal resolution important for a better understanding of the underlying processes.

Soil gas fluxes can be derived from CO2 profiles using the concentration gradient over depth (gradient method) (*De Jong* and *Schappert*, 1972). For applying the gradient method, the specific diffusion coefficient of the soil (*D*S) is needed. *D*S is a gas specific coefficient describing how fast this gas diffuses through a porous medium. *D*S values can be divided by the diffusion coefficient in free air (*D*0) of the specific gas to obtain the dimensionless relative gas diffusion coefficient in soil *D*S/*D*0. *D*S/*D*0 is independent of the gas species and therefore suitable for the comparison of methods that use different gases (*Laemmel* et al., 2017a). Estimation of DS is a major source of uncertainty when the gradient method is used (*Maier* and *Schack-Kirchner*, 2014), since *D*S cannot easily be measured in the field.

*D*S is usually measured with soil cores in the laboratory or transfer functions are used. Laboratory measurements have the disadvantage that normally only small cores are analyzed. On the one hand multiple samples have to be analyzed in order to get representative information about a soil which makes this method laborious. On the other hand soil structures can be disturbed by the sampling procedure, e.g. isolated pores can be opened or pores can be smeared (*Laemmel* et al., 2017a). Especially macrostructures like cracks, stones or large roots are often not represented in sampled soil cores leading to biased results in heterogeneous substrates (*Allaire* et al., 2008).

Transfer functions are often used as an alternative to laboratory measurements, but they often yield large errors and are only reliable for the soils that were used to develop them (*Schack‐Kirchner* et al., 2001). In transfer functions *D*S is often described as a function of the air-filled pore-space (ε, m³ m-³) (*Allaire* et al., 2008). At high water content ε is low leading to low diffusivity. In a dry soil ε is high, leading to high gas transport rates. *Sánchez-Cañete* et al. (2017) calculated soil CO2 fluxes based on several *D*S transfer functions, and compared them with automated chamber measurements. They found poor agreement between the transfer functions and the chamber measurements and therefore suggested to determine *D*S *in situ*.

For measuring *D*S *in situ* different methods have been developed, that often use tracer gases (*Werner* and *Grathwohl*, 2004). Measuring *D*S *in situ* has the advantage that macrostructures are included in the measurement and transport processes other than diffusion can be observed. Many existing set ups for *in situ* measurements of *D*S disturb the soil during installation even more than soil core sampling (*Allaire* et al., 2008).

*Laemmel et al.* (2017a) developed an *in situ* approach for determining *D*S using a sampling device that can be inserted into a predrilled hole with helium as a tracer. While helium is an ideal tracer gas (inert and high *D*0), the precise measurement of helium concentrations below 0.5 % is challenging and requires using laborious techniques such as gas chromatography.

Our objective was to develop and test a mobile system that allows a fast and easy installation. Based on the approach of *Laemmel et al.* (2017a) we developed a new set up to be able to measure with a higher temporal resolution with a simplified measurement design using built-in sensors. To overcome the use of Gas Chromatography we decided to use CO2 as a tracer which can be measured with small infrared sensors. To isolate the tracer CO2 from the natural respiration we developed the differential CO2 profile probe (DCPP) approach. We hypothesize that diurnal patterns of CO2 concentrations in different depths are spatially consistent on the plot scale and therefore CO2 measurements from different locations can be related to each other.

# Material and methods

## The differential CO2 profile probe approach: Technical specifications

We developed the DCPP approach to enable the use of CO2 as a tracer gas in natural soil despite the fact that CO2 is produced in soils by respiration. Two CO2 concentration profiles are measured simultaneously, one profile to observe changes in the natural CO2 profile and another profile where CO2 is injected as a tracer. Tracer CO2 concentrations are then determined by subtracting the natural CO2 profile from the profile where the injection took place. With the resulting tracer profiles *D*S values can be calculated by inverse fitting of a gas diffusion model. To facilitate continuous measurements of soil CO2 profiles we developed a CO2 profile probe that can easily be installed in the soil.

### CO2 profile probe

With our new CO2 profile probe CO2 concentrations can be measured continuously in several depths. CO2 concentrations are measured with nondispersive infrared (NDIR) sensors (MSH2-LP/CO2, Dynament, UK). The sensors are inexpensive, relatively small (diameter: 20 mm; height: 21 mm) and have a low energy demand which makes a set up with multiple sensors affordable regarding costs and energy supply. The measurement range is 0-5000 ppm with a resolution of 10 ppm. A schematic representation of the probe is shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** a.

((Figure 1))

The probe consists of several identical 3D printed segments (diameter: 58 mm; height: 35 mm) that are linked by three pipes which are used as conduit for the electrical wires and additional access tubes. Each segment contains one individual CO2 sensor. The probe consists of 7 segments, so measurement depths are 3.5, 7, 10.5, 14, 17.5, 21 and 24.5 cm. At the measurement depths air inlets allow a diffusive exchange between soil air and the measurement chamber. The sensors are covered with a GORE TEX membrane to protect them from moisture.

For the installation of the probe it is inserted into a hole drilled by a soil auger. To prevent gas bypassing along the wall of the drill hole we equipped each segment with an inflatable gasket between the measurement locations. The gaskets can be inflated through a pressure valve at the top of the probe using a bicycle pump.

A tracer gas can be injected through the probe into the soil to allow *in situ* *D*S measurement. The tracer is inserted into a steel tube that leads from the top segment to the bottom of the probe into the soil (**Fehler! Verweisquelle konnte nicht gefunden werden.** a) bottom). An additional tube connection can be set to one depth to measure different gases with an external gas analyzer. This tube is connected to a permeable hydrophobic membrane tube (Accurel© PP V8/2HF, Membrana GmbH, Germany) that equilibrates with the soil air. This additional connection allows measuring and calculating gas fluxes of other gases than CO2 for example CH4 by using the *in situ* measured *D*S.

### Tracer gas injection

We used CO2 as a tracer, because it has a relatively high *D*0 (0.1381 cm2 s-1 at 0 °C and 1013.3 hPa, (*Massman*, 1998)) and can be considered to be inert in acidic soils. In calcareous soil dissolution of CO2 in water may bias the results of this method, especially under wet conditions. However, after steady state has been reached and gas phase, soil solution and mineral phase are in equilibrium no further dissolution of CO2 should take place if water flow inside the profile can be neglected. CO2 can accurately be measured with small NDIR sensors. The tracer was injected by a peristaltic pump (Ismatec, Wertheim, Germany). Previous experiments showed that diurnal temperature cycles may affect the elasticity of the tubes in the pump which then affect the injection rate. Therefore, the pump was set in an isolated box that was thermally stabilized by a heating device set to a constant temperature to keep the injection rate stable. To prevent mass flow induced by the tracer injection, low injection rates between 0.1 and 0.3 ml per minute were used. In this range of injection rates convective air flow can be neglected (*Laemmel* et al., 2017a). The injection rate directly affects the maximum CO2 concentration which should be kept within the measurement range of the sensors.

Before and after each injection period the injection rate was measured by connecting the injection tube to a closed volume and observing the concentration change over time. The injection rate was then linearly interpolated between these measurements.

### Differential CO2 profile probe approach

Technically, CO2 is an ideal tracer gas in soil because it has a high *D*0 and is not consumed in the soil if substantial dissolution in soil water can be neglected which is the case in in acidic soils. However, CO2 is also produced by soil respiration, which also underlies temporal and spatial variability. To account for these changes in natural CO2 concentrations in the soil, we developed the DCPP approach that allows to separate the tracer CO2 signal from the natural CO2 profile (Fig. 1 b)). Two CO2 profile probes (injection probe and reference probe) are installed with an approximate distance of 1.5 – 5 m. They should not be closer so that the tracer does not affect the reference profile, but close enough to obtain a comparable reference profile.

As soil CO2 concentrations vary in space due to spatial variability of soil respiration and soil moisture and thus gas diffusivity, the reference profile will never exactly resemble the CO2 profile at the injection sampler. To consider this, the natural CO2 profiles have to be measured with both probes before the tracer injection to examine the offset of the two profiles. After this calibration period CO2 is continuously injected into the injection probe while the reference probe still measures the natural CO2 profile. After the injection period a second calibration period should take place to be able to detect a drift in the offset of the CO2 profiles.

The calibration periods were used to fit an offset model that estimates the natural profile at the injection probe with the reference profile as a predictor. For each depth an individual correction model was fitted. We used a generalized additive model (GAM) (*Wood*, 2017) to account for changes in the offset of the two CO2 profiles over time. As the diurnal patterns of the two profiles were differing in some cases the hour of the day was used as a second predictor in the GAM. To separate the tracer signal, the output of the offset model was subtracted from the CO2 concentrations measured at the injection profile.

As an alternative offset model we tested a GAM that describes the CO2 concentration over time as a function of the date and the hour of the day without using the data from the reference probe. This model was used to asses whether or not the reference approach brings an advantage in predicting the natural CO2 profile while injection periods. The two models were compared by dividing the calibration period in training and validation subsets to estimate the model uncertainty for data outside the fitting range.

### Gas transport modelling

The observed tracer profiles were used to fit a gas transport model to estimate the *D*S profile of the soil. We modelled the gas transport with a 2D axisymmetric steady-state model using the finite element modelling software COMSOL (Comsol Multiphysics 5.2a, Burlington, USA). For data processing we used the statistical programming language R (*R Core Team*, 2019)

To model gas transport in the field we defined a sufficiently large cylinder (depth= 1.5 m, diameter = 1.8 m) so that the boundaries of the model did not affect the modelling of the gas profiles. The geometry of the probe was implemented in the center. At the bottom of the injection tube a CO2 source was defined with a constant flux that was set to the tracer injection rate. Bottom and side of the cylinder were defined as no flux boundaries. Above the soil a thin air layer was defined (10 cm). To model CO2 fluxes in COMSOL we only used the tracer CO2 signal, that means the injected CO2 without atmospheric CO2 and CO2 from respiration. Therefore, a constant CO2 concentration of 0 mol­ m-3 was defined at the top of the air layer. The modelled soil was divided into 3 layers (0-10.5 cm, 10.5-21 cm and 21-150 cm depth) to enable different *D*S values over depth. The amount of layers was limited to three so that for each layer CO2 concentrations measured at several depths could be used to fit the model. Diffusion in the soil was assumed to be anisotropic with higher diffusivity in the vertical direction than in the horizontal direction (*Kühne* et al., 2012). We used an anisotropy factor of 1.26 (vertical *D*S / horizontal *D*S) that was derived for the same location by *Maier* et al. (2017). *D*S profiles were derived by fitting the model to the observed tracer profiles using the optimization algorithm SNOPT which is incorporated in the optimization module of COMSOL. The DS values in the model were adjusted by the SNOPT algorithm until the modelled CO2 profile showed the best agreement with the measured profile

## Test and validation of the method

### Laboratory experiments

To test the method under controlled conditions we installed the probe in a bucket filled with different inorganic substrates. We used sand, grit and a mixture of both as substrates. CO2 was injected until steady-state was reached. We repeated the injection twice with each substrate. To model gas transport in the bucket experiments and derive *D*S, we implemented the geometry of the bucket in the COMSOL model.

To compare the results of the gradient method with laboratory results we used the well-established one-chamber method described by *Flühler* (1973), observing the recovery of nitrogen after flushing the chamber with argon (for details see *Maier* and *Lang*, 2019).

CO2 production inside the soil was simulated by additional CO2 injection (*P*sim) at the bottom of the bucket. *P*sim was injected through a membrane tube spiral (Accurel© PP V8/2HF, Membrana GmbH, Germany) that was installed as a layer in the bucket before filling in the substrate. While injecting the CO2 the air inside the membrane tube was permanently circulated to ensure a homogeneous distribution of the CO2 throughout the *P*sim layer. The experiment was done in three steps first only *P*sim than *P*sim + tracer and at last only tracer injection. The tracer signal was calculated by subtracting the CO2 profile from step one from the profile from step two. Step three was used to test if the separation of the tracer signal from *P*sim was accurate.

In a second experiment we injected CO2 in three layers (10, 20 and 40 cm depth) inside the bucket filled with grit to simulate different CO2 production profiles and test if the production profiles can be accurately estimated using the CO2 profile probe. All combinations of the three *P*sim depths were tested to validate the CO2 flux estimation of the method. The injection rates of *P*sim were measured according to the tracer injection rates, before and after each experiment and linearly interpolated. The estimation of the CO2 Production was done with a COMSOL model, as the geometry of the bucket limits the gas transport in the substrate and therefore 1D gas transport cannot fully explain the CO2 distribution in the bucket. The three production layers were implemented inside the COMSOL model and the production rates were inversely estimated by fitting the modelled CO2 profile to the measured CO2 profiles. DS values were taken from the former experiments.

### Field experiments: Estimating soil gas diffusivity

To test the soil CO2 profile probes and evaluate the DCPP approach under field conditions we ran several tests in summer 2020. Field experiments were conducted in a Scots pine forest at the meteorological experimental site in Hartheim (Upper Rhine Valley, southwest Germany). The site is equipped with permanent monitoring infrastructure such as soil moisture and temperature profiles (for details please see *Laemmel* et al., 2017b). The soil is a Haplic Regosol with an Ah Horizon from 0 to 15 cm consisting of loamy silt and a transitional horizon between 15 and 40 cm with less silt and more gravel (for detailed profile description see *Maier* et al., 2010).

The two probes were installed in soil and CO2 dynamics were measured for several days before the first injection experiments to monitor diurnal patterns and temporal drifts in the two profiles. We changed the position of the reference probe twice within a radius of 1.5 to 5 m from the injection probe to get an overview of the spatial heterogeneity of the CO2 dynamics. After this monitoring period CO2 was injected for several days under rainless conditions. Rain events were excluded from the measurements because their effect on the CO2 profiles was very heterogeneous. The periods before and after each injection were used as calibration periods. We repeated this experiment several times to find the optimal injection rate that doesn’t exceed the measuring range of the sensors while still being detectable in the upper soil layers.

To validate the resulting *D*S values, we compared them with *D*S values calculated by a transfer model using the air-filled pore-space (ε):. The coefficients *c* and *d* of the function (f(ε)) were taken from *Maier* et al. (2012). ε was estimated by porosity measurements from *Maier* et al. (2012) and the current soil water content (SWC). SWC probes are installed in three profiles at the experimental site (depths: 5, 10, 20, 50 and 100 cm). The SWC profiles were measured with Aquaflex II probes (UP GmbH, Ibbenbüren, Germany) which were located between 20 and 50 m away from the CO2 profiles. To account for the variability of the measurements f(ε) was calculated for max, min and mean values of the SWC and porosity measurements. As absolute values of in situ soil moisture measurements underly a big uncertainty depending on the sensor type and the calibration for the specific soil (*Jackisch, Conrad* et al., 2018) the interest of using this data lay mostly in the temporal patterns and a rough estimate of the range of SWC.

### Field experiments: Estimating soil gas efflux

We calculated CO2 fluxes (FCO2) (µmol m−2 s-1) based on the measured CO2 profiles and the modelled *D*S values (m2 s-1) assuming Fick’s Law for a one-dimensional profile (Eq. 1):

Eq. 1

With *dc/dz* being the gas concentration gradient (µmol m−3 m-1). FCO2 at the surface was calculated using the measured CO2 gradient between 0 and 7 cm depth and the *D*S value of the topsoil layer that was derived from the diffusion model. Additionally, we calculated FCO2 between 10 and 20 cm using the measured CO2 gradient and the modelled *D*S value.

For the validation of the FCO2 at the surface we conducted closed chamber measurements as a reference. We used four non-steady-state chambers located next to the CO2 profiles probes. PVC collars (diameter 0.17 m, height 0.25 m) were inserted approximately 5 cm into the soil. Chambers were closed for five minutes. CO2 concentrations were measured with a portable gas analyzer (Microportable Gas Analyzer, ABB Inc. Measurement & Analytics, Quebec, Canada). FCO2 between soil surface and atmosphere was calculated by the change of the CO2 concentration in the chamber over time (dc/*dt*) (µmol m−3 s-1) using Eq. 2.

Eq. 2

With *V* being the volume of the chamber system (m3) including the volume of the analyzer and *A* being the base area of the chamber (m2).

We used an empirical transfer model from *Maier* et al. (2011) to estimate a continuous FCO2 signal as an additional reference. With this model FCO2 is calculated using the soil water content (Vol %) at 20 cm depth (SWC20) and the soil temperature (°C) at 3 cm depth (T*3*) (Eq. 3):

Eq. 3

# Results

## Laboratory experiments

The CO2 profile in the bucket experiments reached steady-state after about 10 hours. The CO2 values were increasing with a relatively linear depth gradient (Fig. 2). The observed profiles could be reproduced by the COMSOL diffusion model with R² of around 0.99. The resulting *D*S/*D*0 values for grit and sand were both around 0.25. The mixture of both had the lowest *D*S/*D*0 with 0.16 (Table 1). Replications of the experiment gave very similar results with a standard deviation of around 0.008. Results from the laboratory *DS* measurements of the different substrates were similar to the results of the *in situ* method. *D*S/*D*0 of sand and grit were around 0.04 higher for the *in situ* method while the mixture of both had almost the same result for both methods. The tracer profiles from the experiments with additional *P*sim agree well with the tracer profiles measured without *P*sim (R2 0.99) (Fig 2 a).

((Figure 2))

((Table 1))

The production profiles estimated with the COMSOL model showed good agreement with the known injection rates of *P*sim (R2 0.72) (Fig. 3). While *P*sim in depth 1 and 3 tended to be underestimated *P*sim in depth 2 tended to be overestimated. For each experiment also the sum of *P*sim across the whole profile was calculated. The totalized values of the model agreed even better with the known injection rates (R2 0.97).

((Figure 3))

## Field experiments

The field experiments were conducted after a very dry early summer period interrupted by isolated intense rain events. The rain events led to abrupt rises in SWC of the topsoil while the subsoil stayed constantly dry throughout the experimental period (Fig. 4).

The CO2 profiles measured in the field showed a clear CO2 gradient increasing with depth. The CO2 concentrations showed diurnal patterns with higher values in the evening and night and its minimum around midday analog to the soil temperature at 20 cm depth. CO2 concentrations in the lower depths reached extremely high values and sometimes exceeded the measurement range of the sensors. As a response to precipitation soil CO2 concentrations were rising abruptly. After the abrupt increase due to rain CO2 concentrations were slowly decreasing analog to the decrease in SWC. Before the first two injection periods (shaded grey area in Fig. 3) an intense rain event led to very high CO2 concentrations in the soil. The reaction to rain differed between the two observed profiles. The reference profile showed a stronger increase in CO2 after rainfall and a steeper decrease in the following days.

((Figure 4))

The CO2 depth profiles at the different positions exhibited a big spatial heterogeneity (Fig. 5). However, diurnal patterns in the different depths were comparable at all Position pairs. In the deeper soil CO2 dynamics showed clear sinusoidal patterns while in the upper soil diurnal patterns were more complex.

((Figure 5))

## Data processing and modelling

The reference profile adjusted by the *GAM* could reproduce the injection profile during the calibration periods with R2 between 0.999 and 0.905 for the different depths. The alternative offset model that was fitted without using the reference data could also be used for short time periods but gave worse predictions for the validation dataset. Additionally, the diurnal patterns in the upper soil are quite variable which makes it difficult to fit a model just using the time as predictor and raises the probability of creating artifacts. Using the reference data could improve the accuracy in predicting the tracer concentrations, especially in the upper soil layers.

After calibrating the offset model, it was used to estimate the natural CO2 profile at the injection probe during the injection periods. In the deeper layers a clear tracer signal could be extracted by subtracting the adjusted reference CO2 values. For the upper layers the derived tracer signal was less stable, as the tracer concentration was small (0-200 ppm) compared to the natural CO2 concentration (600-1200 ppm) and the resolution of the CO2 sensors (10 ppm). To optimize the configuration of the set-up the injection rate was increased stepwise after the first injection periods. The injection with the highest injection rate (0.26 ml min-1) showed the clearest tracer signal in the top layer. The resulting tracer profiles showed an exponential CO2 gradient with depth.

The modelled *D*S values showed a clear profile with higher *D*S values close to the surface and lower *D*S values in the deeper soil (Fig. 6 top). The *D*S/*D*0 of the upper layer (*D*S/*D*01) ranged from 0.32 to 0.89, values in the second layer (*D*S/*D*02) ranged from 0.16 to 0.21, and in the bottom layer (*D*S/*D*03) values lay between 0.07 and 0.08.

DS/D01 showed strong fluctuations due to a weak tracer signal in the topsoil that was in the range of the limited precision of the DCPP approach. This resulted in a high uncertainty in isolating the tracer signal. To improve the detection of the tracer signal and stabilize the estimation of *D*S/*D*01 we aggregated the data using a moving average. The window size of the moving average was increased until a steady tracer profile was reached. The first injection was rejected because no stable tracer profile could be reached. The tracer profile of the second injection could be stabilized by a moving average of 12 hours. In the deeper layers, the modelled DS/D0 values (DS/D02 and DS/D03) are quite stable over time for all injection rates indicating a higher precision of the tracer separation and the gas diffusion model.

The *D*S/*D*0 values for the upper two layers show a good agreement with the *D*S values calculated with f(ε). The *D*S value of the subsoil was lower with the *in situ* approach than with the transfer model. However, the results of f(ε) underlie big uncertainties (shaded areas in Fig. 5) as the used SWC and porosity values spanned over a wide range and the exact values were not available for the exact location of the CO2 profiles.

((Figure 5))

The calculated surface CO2 fluxes ranged from 1.5 to 4.9 µmol m-2 s-1. They agree with the results from the chamber measurements indicating that DS/D01 is in a realistic range. FC02 also agrees well with the results from the transfer function from *Maier* et al. (2011). For the second injection the diurnal patterns of the transfer function are very close to our results. At the last injection the results from the gradient method lay below the estimates of the transfer function but still at the border of the uncertainty range estimated by the uncertainty of the input parameters of the transfer function (SWC20 and T3). The CO2 fluxes between 10 and 20 cm that were calculated using *D*S/*D*02 lay constantly below the surface effluxes and made 70 % of the surface efflux on average.

((Figure 6))

# Discussion

probe

The CO2 profile probe could easily be installed in the soil and CO2 profiles could be measured already a few hours after installation. Using a multilevel probe allows assigning CO2 concentrations precisely to measurement depth compared to approaches with several dug in CO2 probes which usually includes an uncertainty of 1-2 cm (*Maier* et al., 2011; *Vargas* et al., 2010; *Tang* et al., 2003).

dcpp Similar approaches

With the DCPP approach we could measure the natural soil CO2 profile and determine *D*S values *in situ* which allowed calculating CO2 fluxes directly without any further measurements necessary.

Similar approaches have been presented in other studies (*Laemmel* et al., 2017a; *van Bochove* et al., 1998; *Werner* and *Grathwohl*, 2004). *Werner* and *Grathwohl* (2004) describe several set-ups for *in situ* measurements of *D*S, but most of these set-ups are only used for single *D*S measurements and not for monitoring of *D*S changes over time. *Van Bochove* et al (1998) and *Laemmel et al.* (2017a) developed approaches that enable the monitoring of *D*S changes over time using N2O and helium as a tracer, respectively. While helium and CO2 both have high *D*0 values N2O has a much lower diffusivity; it takes over two days to reach steady-state which limits the temporal resolution of the measurements (*van Bochove* et al., 1998). Helium has the advantage of being an inert gas, which is not produced or consumed in the soil. In our study we used CO2 for practical reasons. CO2 can accurately be measured with small and affordable NDIR sensors which allows to overcome cumbersome analytical equipment like gas chromatography. By including NDIR sensors directly in the probe all depths could be measured at the same time while with the set-up of *Laemmel et al.* (2017a) the depths had to be measured successively. This enables a much higher temporal resolution than in former studies which allows the identification of short-term effects.

Lab tests Porductionseimer

To test the accuracy of the estimation of DS and PCO2 profiles with this method under controlled conditions the first experiments were conducted in a bucket with homogeneous inorganic substrates. The results for DS agreed well with results from laboratory measurements with soil cores of the same substrates. Differences in a similar range have been found by other comparisons of *in situ* and laboratory methods for *D*S measurements (*Laemmel* et al., 2017a).

Also the accuracy of the PCO2 profile estimation was satisfying under controlled conditions. The measured CO2 profiles could successfully be used to fit a 3D gas diffusion model and reproduce the known *P*sim rates. To be able to identify a CO2 source profile from a CO2 concentration profile the source distribution function should be known as (*Novak*, 2007) demonstrated in his theoretical work. In our case the CO2 production doesn’t follow a continuous function but was limited to 3 discrete layers.

In a natural soil the CO2 source distribution is not known which raises the uncertainty of the estimation. As frequently done in other studies we calculated FCO2 for discrete layers with linear gradients (*Fierer* et al., 2005; *Schwendenmann* and *Veldkamp*, 2006). As (*Koehler* et al., 2010) pointed out, for a mathematical correct calculation a continuous function should be fitted to the CO2 profile, and the separation into discrete layers is somewhat arbitrary. However, also the choice of the continuous function can change the result several fold (*Koehler* et al., 2010). Either way the high spatial resolution of the CO2 measured with our probe represents a good base for fitting either a continuous function or discrete linear gradients.

Heterogeneity

The heterogeneity of the CO2 profiles at the different locations of the reference probe emphasizes the need of the calibration periods before and after each injection. The data from the different positions illustrates that the diurnal patterns in the different depth layers are quite consistent over space even if the absolute values and the temporal drift over several days differ strongly. This verifies our hypothesis that a reference probe can be a good predictor for the CO2 profile while the tracer injection periods. The main drivers for CO2 dynamics in soil are SWC which has a strong influence on DS (*Allaire* et al., 2008) and T which mainly controls PCO2 (*Jassal* et al., 2004; *Novak*, 2007). SWC is spatially variable, especially after rain events (*Famiglietti* et al., 1998; *Van den Pol-van Dasselaar* et al., 1998) but in rainless periods only changes slowly over time depending on soil water retention properties. SWC is probably the driver for the temporal drift that was observed in the two CO2 profiles. T shows sinusoidal diurnal patterns that can be expected to be quite persistent over space which might explain the spatial consistency of the diurnal patterns of the CO2 concentrations. The complexity of the diurnal patterns in the upper soil suggests that also other meteorological factors like wind have a strong influence on the gas exchange in the upper soil.

DCPP limitations

The results from the field experiments showed that the DCPP approach is generally applicable for relatively homogeneous soils. However, the results illustrate clear challenges and limitations for the DCPP approach. For reliable predictions of *D*S with this method no rain events should occur at least three to four days before and after the injection because of the heterogeneous reaction of the CO2 profiles due to respiration pulses as documented in other studies (*Tang* et al., 2005; *Xu* et al., 2004). Injection should be switched off every 3-5 days until a comparison of the natural soil CO2 profiles can be achieved so that the adjustment of the reference profile is representative for the whole injection period.

Feps comparison

The comparison of the results of the *in situ* method with the transfer function f(ε) indicated that *D*S/*D*0 values lay in a realistic range, only *D*S/*D*03 was outside the range of f(ε). The value of *D*S/*D*03, however, represents the widest depth range from -20 cm down to the lower limit of the model that was set to -150 cm.

DSD01 injection closer to surface

Estimations of *D*S/*D*01 underlay the biggest fluctuations. It is unclear to which degree diurnal patterns in *D*S/*D*01 were caused by natural processes (e.g. effects due to wind or solar radiation on the humus layer) and to which degree they were artifacts from the CO2 profile adjustment and model uncertainty. *Maier* et al. (2017) described similar uncertainties in modelling gas transport of the upper soil, which are attributed to low concentration gradients and high *D*S/*D*0 values in the topsoil. To overcome the uncertainty in estimating *D*S/*D*0 of the upper soil the experimental design could be adjusted by using a shorter probe and increasing the injection rate which would lead to a clearer tracer signal in the topsoil. *Laemmel et al.* (2017a) presented a similar adjustment for their set-up yielding better estimates for *D*S/*D*0 of the topsoil with the injection closer to the surface.

Chamber calibration

*Sánchez-Cañete et al.* (2017) suggested to use chamber measurements to calibrate the *D*S model that is used for the gradient method. Calibration of the *D*S with chamber measurements has the advantage that respiration between the measurement depths is included (*Sánchez-Cañete* et al., 2017). We did not calibrate our modelled DS values with the chamber measurements as we wanted to test if the method is applicable without further measurements. Chamber measurements were just used to validate the results of FCO2. Although we did not use the chamber measurement to calibrate our modelled *D*S values, chamber measurements showed good agreement with the results from the gradient method.

# Conclusions

The results presented in this study support the hypothesis that reference CO2 measurements are a good predictor for the CO2 dynamics at the injection probe. Although spatial heterogeneity of the absolute values and the temporal drift of the CO2 concentrations makes a careful calibration of an offset model necessary. Therefore, a continuous tracer injection over longer time periods was not possible under the conditions of the presented field tests, especially if rain events occurred. For injection periods between two and five days derived DS and FCO2 values agreed well with established laboratory and field methods for depths up to 20 cm. Nevertheless, the application of the DCPP approach underlies several limitations. If those limitations are carefully addressed this method allows an efficient way to investigate soil gas transport phenomena and soil respiration profiles.

The CO2 profile probe showed good performance and provided reliable data with small energy consumption. Since the developed probe can easily be installed in the soil different locations can be compared without big effort and short-term effects can be investigated. Its possible applications range from monitoring of CO2 concentration profiles, over *in situ* *D*S measurements using the DCPP approach to estimate soil respiration and deriving CO2 flux profiles using the gradient method.

ALT test 2

We presented a *Differential CO2 Profile Probe* approach to measure soil gas diffusivity and soil respiration profiles *in situ*. Derived *D*S/*D*0 values for 0-20 cm depth agreed well with established laboratory and field methods. Comparison with chamber measurements showed that surface CO2 efflux could accurately be estimated using the derived *D*S values and the CO2 gradient over depth. Also, soil CO2 flux at 10 cm depth could be derived allowing to estimate the contribution of different soil layers to total soil respiration. However, the application of the DCPP approach underlies several limitations. If those limitations are carefully addressed this method allows an efficient way to investigate soil gas transport phenomena and soil respiration profiles.

The CO2 profile probe showed good performance and provided reliable data with small energy consumption. Since the developed probe can easily be installed in the soil different locations can be compared without big effort and short-term effects can be investigated. Its possible applications range from monitoring of CO2 concentration profiles, over *in situ* *D*S measurements using the DCPP approach to estimate soil respiration and deriving CO2 flux profiles using the gradient method.

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# References

*Allaire, S. E., Lafond, J. A., Cabral, A. R., Lange, S. F.* (2008): Measurement of gas diffusion through soils: comparison of laboratory methods. *J. Environ. Monit.* 10, 1326.

*Bowling, D. R., Massman, W. J.* (2011): Persistent wind-induced enhancement of diffusive CO2 transport in a mountain forest snowpack. *J. Geophys. Res.* 116, G04006.

*Clements, W. E., Wilkening, M. H.* (1974): Atmospheric pressure effects on 222Rn transport across the earth‐air interface. *J. Geophys. Res.* 79, 5025–5029.

*De Jong, E., Schappert, H. J. V.* (1972): Calculation of soil respiration and activity from CO2 profiles in the soil. *Soil Sci.* 113, 328–333.

*Famiglietti, J. S., Rudnicki, J. W., Rodell, M.* (1998): Variability in surface moisture content along a hillslope transect: Rattlesnake Hill, Texas. *J. Hydrol.* 210, 259–281.

*Fierer, N., Chadwick, O. A., work(s):, S. E. T. R.* (2005): Production of ${\rm CO}\_{2}$ in Soil Profiles of a California Annual Grassland. *Ecosystems* 8, 412–429.

*Flühler, J.* (1973): Sauerstoffdiffusion im Boden. *Mitteilungen Schweiz. Anst. Für Forstl. Vers.*

*Jackisch, Conrad, Andrä, Ines, Germer, Kai, Schulz, Katrin, Schiedung, Marcus, Haller-Jans, Jaqueline, Schneider, Jonas, Jaquemotte, Julia, Helmer, Philipp, Lotz, Leander, Graeff, Thomas, Bauer, Andreas, Hahn, Irene, Sanda, Martin, Kumpan, Monika, Dorner, Johann, de Rooij, Gerrit, Wessel-Bothe, Stefan, Kottmann, Lorenz, Schittenhelm, Siegfried, Durner, Wolfgang* (2018): Soil moisture and matric potential - An open field comparison of sensor systems, supplement to: Jackisch, Conrad; Germer, Kai; Graeff, Thomas; Andrä, Ines; Schulz, Katrin; Schiedung, Marcus; Haller-Jans, Jaqueline; Schneider, Jonas; Jaquemotte, Julia; Helmer, Philipp; Lotz, Leander; Bauer, Andreas; Hahn, Irene; Sanda, Martin; Kumpan, Monika; Dorner, Johann; de Rooij, Gerrit; Wessel-Bothe, Stefan; Kottmann, Lorenz; Schittenhelm, Siegfried; Durner, Wolfgang (2020): Soil moisture and matric potential- an open field comparison of sensor systems. Earth System Science Data, 12(1), 683-697.

*Jassal, R. S., Black, T. A., Drewitt, G. B., Novak, M. D., Gaumont-Guay, D., Nesic, Z.* (2004): A model of the production and transport of CO2 in soil: predicting soil CO2 concentrations and CO2 efflux from a forest floor. *Agric. For. Meteorol.* 124, 219–236.

*Koehler, B., Zehe, E., Corre, M. D., Veldkamp, E.* (2010): An inverse analysis reveals limitations of the soil-CO&lt;sub&gt;2&lt;/sub&gt; profile method to calculate CO&lt;sub&gt;2&lt;/sub&gt; production and efflux for well-structured soils. *Biogeosciences* 7, 2311–2325.

*Kühne, A., Schack‐Kirchner, H., Hildebrand, E. E.* (2012): Gas diffusivity in soils compared to ideal isotropic porous media. *J. Plant Nutr. Soil Sci.* 175, 34–45.

*Laemmel, T., Maier, M., Schack-Kirchner, H., Lang, F.* (2017a): An *in situ* method for real-time measurement of gas transport in soil: Monitoring of gas transport in soil. *Eur. J. Soil Sci.* 68, 156–166.

*Laemmel, T., Mohr, M., Longdoz, B., Schack-Kirchner, H., Lang, F., Schindler, D., Maier, M.* (2019): From above the forest into the soil – How wind affects soil gas transport through air pressure fluctuations. *Agric. For. Meteorol.* 265, 424–434.

*Laemmel, T., Mohr, M., Schack-Kirchner, H., Schindler, D., Maier, M.* (2017b): Direct Observation of Wind-Induced Pressure-Pumping on Gas Transport in Soil. *Soil Sci. Soc. Am. J.* 81, 770–774.

*Maier, M., Lang, V.* (2019): Gas Diffusivity in the Forest Humus Layer: *Soil Sci.* 184, 13–16.

*Maier, M., Longdoz, B., Laemmel, T., Schack-Kirchner, H., Lang, F.* (2017): 2D profiles of CO2, CH4, N2O and gas diffusivity in a well aerated soil: measurement and Finite Element Modeling. *Agric. For. Meteorol.* 247, 21–33.

*Maier, M., Mayer, S., Laemmel, T.* (2019): Rain and wind affect chamber measurements. *Agric. For. Meteorol.* 279, 107754.

*Maier, M., Schack-Kirchner, H.* (2014): Using the gradient method to determine soil gas flux: A review. *Agric. For. Meteorol.* 192–193, 78–95.

*Maier, M., Schack-Kirchner, H., Aubinet, M., Goffin, S., Longdoz, B., Parent, F.* (2012): Turbulence Effect on Gas Transport in Three Contrasting Forest Soils. *Soil Sci. Soc. Am. J.* 76, 1518–1528.

*Maier, M., Schack-Kirchner, H., Hildebrand, E. E., Holst, J.* (2010): Pore-space CO2 dynamics in a deep, well-aerated soil. *Eur. J. Soil Sci.* 61, 877–887.

*Maier, M., Schack-Kirchner, H., Hildebrand, E. E., Schindler, D.* (2011): Soil CO2 efflux vs. soil respiration: Implications for flux models. *Agric. For. Meteorol.* 151, 1723–1730.

*Massman, W. J.* (1998): A review of the molecular diffusivities of H2O, CO2, CH4, CO, O3, SO2, NH3, N2O, NO, and NO2 in air, O2 and N2 near STP. *Atmos. Environ.* 32, 1111–1127.

*Novak, M. D.* (2007): Determination of soil carbon dioxide source-density profiles by inversion from soil-profile gas concentrations and surface flux density for diffusion-dominated transport. *Agric. For. Meteorol.* 146, 189–204.

*R Core Team* (2019): A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

*Rey, A., Belelli‐Marchesini, L., Were, A., Serrano‐ortiz, P., Etiope, G., Papale, D., Domingo, F., Pegoraro, E.* (2012): Wind as a main driver of the net ecosystem carbon balance of a semiarid mediterranean steppe in the south east of Spain. *Glob. Change Biol.* 18, 539–554.

*Sánchez-Cañete, E. P., Scott, R. L., van Haren, J., Barron-Gafford, G. A.* (2017): Improving the accuracy of the gradient method for determining soil carbon dioxide efflux: Accurate Long-Term *F*soil Based on the GM. *J. Geophys. Res. Biogeosciences* 122, 50–64.

*Scanlon, B. R., Nicot, J. P., Massmann, J. W.* (2002): Soil gas movement in unsaturated systems. *Soil Phys. Companion* 389, 297–341.

*Schack‐Kirchner, H., Gaertig, T., v. Wilpert, K., Hildebrand, E. E.* (2001): A modified McIntyre and Phillip approach to measure top‐soil gas diffusivity in‐situ. *J. Plant Nutr. Soil Sci.* 164, 253–258.

*Schlesinger, W. H., Andrews, J. A.* (2000): Soil respiration and the global carbon cycle. *Biogeochemistry* 48, 7–20.

*Schwendenmann, L., Veldkamp, E.* (2006): Long-term CO 2 production from deeply weathered soils of a tropical rain forest: evidence for a potential positive feedback to climate warming. *Glob. Change Biol.* 12, 1878–1893.

*Smith, K. A., Ball, T., Conen, F., Dobbie, K. E., Massheder, J., Rey, A.* (2003): Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 54, 779–791.

*Smith, K. A., Ball, T., Conen, F., Dobbie, K. E., Massheder, J., Rey, A.* (2018): Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 69, 10–20.

*Takle, E. S., Massman, W. J., Brandle, J. R., Schmidt, R. A., Zhou, X., Litvina, I. V., Garcia, R., Doyle, G., Rice, C. W.* (2004): Influence of high-frequency ambient pressure pumping on carbon dioxide efflux from soil. *Agric. For. Meteorol.* 124, 193–206.

*Tang, J., Baldocchi, D. D., Qi, Y., Xu, L.* (2003): Assessing soil CO2 efflux using continuous measurements of CO2 profiles in soils with small solid-state sensors. *Agric. For. Meteorol.* 118, 207–220.

*Tang, J., Misson, L., Gershenson, A., Cheng, W., Goldstein, A. H.* (2005): Continuous measurements of soil respiration with and without roots in a ponderosa pine plantation in the Sierra Nevada Mountains. *Agric. For. Meteorol.* 132, 212–227.

*van Bochove, E., Bertrand, N., Caron, J.* (1998): In Situ Estimation of the Gaseous Nitrous Oxide Diffusion Coefficient in a Sandy Loam Soil. *Soil Sci. Soc. Am. J.* 62, 1178–1184.

*Van den Pol-van Dasselaar, A., Van Beusichem, M. L., Oenema, O.* (1998): Effects of soil moisture content and temperature on methane uptake by grasslands on sandy soils. *Plant Soil* 204, 213–222.

*Vargas, R., Baldocchi, D. D., Allen, M. F., Bahn, M., Black, T. A., Collins, S. L., Yuste, J. C., Hirano, T., Jassal, R. S., Pumpanen, J., Tang, J.* (2010): Looking deeper into the soil: biophysical controls and seasonal lags of soil CO2 production and efflux. *Ecol. Appl.* 20, 1569–1582.

*Werner, D., Grathwohl, P.* (2004): Review of Field Methods for the Determination of the Tortuosity and Effective Gas-Phase Diffusivity in the Vadose Zone. *Vadose Zone J.* 3, 9.

*Wood, S. N.* (2017): Generalized additive models: an introduction with R. CRC press.

*Xu, L., Baldocchi, D. D., Tang, J.* (2004): How soil moisture, rain pulses, and growth alter the response of ecosystem respiration to temperature: RAIN, GROWTH, AND RESPIRATION. *Glob. Biogeochem. Cycles* 18, n/a-n/a.

# Tables

**Table 1:** Mean *D*S/*D*0 values from the laboratory measurements (Lab) and the in situ measurements (sd in brackets).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Substrate | *in situ* *D*S/*D*0 | Lab *D*S/*D*0 | Mineralogy | particle size |
| sand | 0.24 (0.006) | 0.21 (0.006) | quartz | 0.063 – 0.63 mm |
| grit | 0.26 (0.009) | 0.22 (0.015) | granite | 3 - 10 mm |
| mixture | 0.16 (0.008) | 0.16 (0.015) | quartz, granite | 0.063 – 10 mm |

# Figures

**Figure 1:** a) Schematic representation of the CO2 profile probe. b) Schematic representation of the DCPP approach. CO2 concentrations in the soil are illustrated as a color gradient from red (high concentration) to blue (low concentration).

**Figure 2:**a) Visualization of the COMSOL model that was used to simulate gas diffusion in the bucket experiments. b) observed (obs) and modelled (mod) CO2 profiles in the different substrates at steady‑state.

**Figure 3:** Production …

**Figure 4:** Field experiment: Time series of the CO2 profiles of a) the injection and b) the reference probe show diurnal patterns and strong reactions to increases in soil moisture. Injection periods are shaded in grey. c) Time series of volumetric soil water content (SWC, left axis) and precipitation (P24h moving total over last 24 h, right axis). A fast response of SWC after rainfall can be observed in the topsoil, while the SWC of the subsoil remains at the same level. d) Time series of the soil temperature (Soil T) for the different depths.

**Figure 5:** Time series of the isolated tracer concentration profile (CO2 tracer) for the three injection periods. Injection rates were increased from 0.07 (injection 1) over 0.17 (injection 2) to 0.26 ml min-1 (injection 3).

**Figure 6:** Time series of modelled *D*S values of the 3 layers of the diffusion model. *D*S/*D*01 values of the first injection were rejected because no steady tracer profile could be reached. Values of the second injection were smoothed by a moving average over 12 hours to stabilize the estimation of *D*S/*D*01. As a reference the *D*S values of the transfer function f(ε) are shown with their uncertainty range signed as shaded area.

**Figure 6:** Time series of CO2 fluxes (FCO2) at the soil surface and below 10 cm. Comparison of the model results using the gradient method with *D*S values from the DCCP approach and chamber measurements from four chambers. Estimates of FCO2 by a transfer function from *Maier* et al. (2011) are included as dashed line.