Are the hydrophobic membrane tubes suitable for instantaneous soil CO$_2$ concentration measurements?

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Received 28 April 2017; revised 24 July 2017

One technique for measurement of soil CO$_2$ production and emission is a gradient method using CO$_2$ concentration measurements within soil by polypropylene membrane tubes (Accurel® PP V8/2 HF). In this study, we determined whether these tubes are suitable for monitoring instantaneous CO$_2$ concentration and its rapid changes in the soil. The tested tube was placed within the plastic bag. The CO$_2$ concentration was continuously measured in both the tube and the bag to determine the time lag in CO$_2$ concentration changes in the tube after an evoked rapid increase in CO$_2$ concentration in the bag. We found that higher the CO$_2$ concentration and higher the increase in CO$_2$ concentration around the tube, the faster is the change in CO$_2$ concentration within the tube. These relationships were described by hyperbola models and corresponding equations. Our results confirm that the tested membrane tubes are suitable for monitoring rapid changes in soil CO$_2$ concentration.

[Keywords: Carbon dioxide, accurel tubes, gradient method, soil profile, polypropylene]

Introduction

Recent great interest in soil processes has led to a number of studies focused on gas exchange between soil and atmosphere. These studies have been mostly focused on CO$_2$ as it is an important green-house gas and its losses from soil represents a crucial role in the global carbon cycle. The most common field methods for monitoring CO$_2$ fluxes are: Eddy-covariance method, chamber methods and gradient method.

Recently, the use of gradient method has increased as it may also help to determine where the carbon sources and sinks are situated within the soil profile. The gradient method is based on measurements of gas concentrations in different depths of the soil and transport properties (such as soil porosity, aggregation and structure, temperature, and water content). Soil gas (soil air) moves out into the atmosphere mainly due to displacement by the incoming water and by the water level fluctuation. The final movement of individual gas species is regulated by the partial pressure under which it exists. In the soils, the dynamic equilibrium is established as a result of mass flow and diffusion of gas mixture in the soil profile. The gas is transported in the medium by diffusion from places with higher gas concentration to places with lower gas concentration. The rate of the transport depends on the difference of the concentration and on the gas diffusivity of the porous medium.

There are two basic systems of soil gas sampling. The first, so called active system, draws air actively from the air-filled pore space directly by a syringe or from tubes. The tubes through which the soil air is drawn can be installed directly in the soil surface, buried at certain depths, or installed into the wall of a soil pit. The sampling tubes are usually metal tubes and have a perforated a lower end. The second system, passive in nature, measures gas concentration using sampling tubes or sensors that are allowed to equilibrate with the soil air. Using the passive sampling systems, it is possible to limit disturbances to the natural soil gas environment. The material of tubing is required to be fully permeable for a traced gas, but completely hydrophobic. The rate of equilibration of CO$_2$ concentration between the tubing and soil air is a crucial parameter to state if the measured concentration is immediate or changes with some time lag. Changes in soil CO$_2$ concentration are usually gradual with diurnal and seasonal patterns with higher dynamics in shallow layers compared to the deep ones. However, sometimes sudden rapid changes may occur, especially after rain events, and these should be defined at the right time.
One of the most used tubes for the gradient method are Accurel® tubes (Membrana GmbH., Wuppertal, Germany) which meet the requirements. The aims of our study were: i) to determine the rate of CO₂ concentration equilibration between inner and outer space of the Accurel tubes (which are standardly used for soil CO₂ concentration measurements) after a rapid increase in CO₂ concentration in the outer space, ii) to determine effect of the magnitude of CO₂ concentration and concentration increase in the outer space on this rate, and iii) to determine whether the tested tubing is suitable for measurements of instantaneous CO₂ concentration and its rapid changes in the soil.

Materials and Methods

In this study, Accurel® PP V8/2 HF tube (Membrana GmbH, Wuppertal, Germany) was tested. The tube parameters are summarized in Table 1. The 20 cm long Accurel tube was kept in a transparent gas tight plastic bag made of polyamide and polyethylene (the wall thickness of 90 µm). The bag and the tube were separately connected to two CO₂ analyzers Li-8100 (Li-Cor Inc., Lincoln, USA) as shown in Figure 1. The air from the tube or the bag was sucked into the analyzer and returned to the tube or the bag. In this way, two closed gas systems were established.

The experiment was realized using a plastic bag that helps in keeping air pressure inside and the surrounding atmosphere at the same level.

The CO₂ concentration in the tube and the bag was continuously measured at the same time in the one-second step. Air with CO₂ concentration from 1500 to 5200 ppm was injected into the internal space of the gas bag using a 150 ml plastic syringe. The gaseous mixing after adding CO₂ enriched air was monitored for CO₂ concentration increase and following concentration stabilization. This was repeated four times in three-minute intervals to allow full equilibration of CO₂ concentration. Then the air from the bag was pushed out and refilled with air of ambient CO₂ concentration. After re-equilibration of CO₂ concentration in the bag, the measurements were repeated. As the concentration in the bag increased after each injection, the initial concentration before the following injection ranged between 500 and 4700 ppm.

Time needed for CO₂ concentration in the tube to reach CO₂ concentration in the bag \(T_{lag}\) was defined as time between the CO₂ concentration peak in the gas bag after the CO₂ injection and time when difference in CO₂ concentration in the gas bag and the tube was not higher than 9 ppm (Fig. 2). This threshold was always less than 0.75% of total concentration within the gas bag, which was in range of 1500 to 5200 ppm of CO₂.

This study analyzed the relationship between \(T_{lag}\) and CO₂ concentration in the bag after the equilibration of CO₂ concentration and the relationship between \(T_{lag}\) and difference in CO₂ concentration before and after the injection of the air with high CO₂ concentration air into the bag. Several models for the relationships were tested:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Accurel PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer type</td>
<td>polypropylene</td>
</tr>
<tr>
<td>Inner diameter (mm)</td>
<td>5.50</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>1.55</td>
</tr>
<tr>
<td>Nominal pore size (µm)</td>
<td>0.20</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>73</td>
</tr>
</tbody>
</table>

Fig. 1 — A scheme of the experiment set up. a - an Accurel

Fig. 2 — CO₂ concentration in the bag and in the tube following each injection of high CO₂ concentration air into the bag. Horizontal dashed lines indicate the period for \(T_{lag}\) calculations.
A polynomial of the first, second, third and fourth order, a hyperbola of the first, second, third and fourth order, a logarithmic equation (with linear polynomial in argument), and a square root of polynomial of the first, second, third and fourth order. For each model, several statistics were determined: MSE (Mean square error), RMSE (Root mean square error), RRMSE (Relative root mean square error), bias, MAW (Mean absolute error), and $R^2$. On the base of these coefficients the best model was chosen for each relationship. The significance of the relationships was tested using F-test at the level of probability $\alpha=0.05$. $T_{lag}$ calculations and statistical analyses were run in the program $R$.

**Results**

After the injection of the air with high CO$_2$ concentration, the analyzer detected fast increase in CO$_2$ concentration in the bag with a sharp peak level several hundred ppm higher than before the air injection. Consequently, CO$_2$ concentration gradually decreased till it reached a constant level as a result of even mixing of the air in the bag (Fig. 2).

The CO$_2$ concentration in the Accurel tube responded to the air injection into the bag a few seconds later than in the bag. The increase in CO$_2$ concentration in the tube was sharp at the beginning and then slowly declined and remained constant after reaching CO$_2$ concentration in the bag (Fig. 2). The time interval when CO$_2$ concentration in the tube reached CO$_2$ concentration in the bag ($T_{lag}$) ranged from 29 to 71 s.

$T_{lag}$ significantly decreased with both the constant CO$_2$ concentration reached after the injection of the air with high CO$_2$ concentration and the difference in CO$_2$ concentration in the bag before and after the injection (Fig. 3). Generally, higher the CO$_2$ concentration and higher the change in CO$_2$ concentration around the tube, the faster was the change in CO$_2$ concentration within the Accurel tube. The best model fitting the first correlation was hyperbola (Fig. 3A) characterized by an equation:

$$y = \frac{265957}{x+3} \quad \ldots (1)$$

The best model for the second correlation was also hyperbola (Fig. 3B) characterized by an equation:

$$y = \frac{146064}{x+2} \quad \ldots (2)$$

Statistics for these models are summarized in Table 2.

**Discussion**

The gradient method is one of the methods being increasingly used for determining CO$_2$ production in the soil$^4$. For precise gradient measurements of CO$_2$ in soil profile, tubes with fully permeable membrane for CO$_2$ can be used.

Table 2 — Statistics of the models of the relationship between time needed for CO$_2$ concentration in the tube to reach CO$_2$ concentration in the bag ($T_{lag}$) and CO$_2$ concentration in the bag after this equilibration ($T_{lag}$ x CO$_2$), and $T_{lag}$ and difference in CO$_2$ concentration before and after injection of high CO$_2$ concentration air into the bag ($T_{lag}$ x difCO$_2$).

<table>
<thead>
<tr>
<th>$T_{lag}$ x CO$_2$</th>
<th>$T_{lag}$ x difCO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model</strong></td>
<td>$y=265957/(x+3189)$</td>
</tr>
<tr>
<td>MSE</td>
<td>24.36</td>
</tr>
<tr>
<td>RMSE</td>
<td>4.93</td>
</tr>
<tr>
<td>RRMSE</td>
<td>0.10</td>
</tr>
<tr>
<td>BIAS</td>
<td>0.02</td>
</tr>
<tr>
<td>MAE</td>
<td>3.81</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.76</td>
</tr>
<tr>
<td>F-value</td>
<td>58.0</td>
</tr>
<tr>
<td>p-value</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

Fig. 3 — Relationship between $T_{lag}$ (time needed for CO$_2$ concentration in the tube to reach CO$_2$ concentration in the bag) and CO$_2$ concentration in the bag after this equilibration (A); and between $T_{lag}$ and difference in CO$_2$ concentration before and after injection of high CO$_2$ concentration air into the bag. Used statistics are summarized in Table 2.
This study evaluated the applicability of the membrane tubes for soil CO₂ concentration monitoring. The suitability of Accurel tubes as a tool to determine CO₂ concentration in the soil was accepted by the study and the measurements with the Accurel tubes allowed to monitor temporal and spatial variation in soil CO₂ concentration and production in individual horizons, to determine soil CO₂ storage or soil CO₂ fluxes.

The results of our study show that due to the rapid response of CO₂ concentration in the tubes on changes in CO₂ concentration of outer space, the Accurel tubes are highly suitable for monitoring of temporal fluctuation in soil CO₂ concentration. Although the temporal dynamics of CO₂ concentration in pore space is usually low and gradual, the tubes for CO₂ concentration measurement do not necessarily need to have any extremely fast response to changes of CO₂ concentration. This is valid especially for deeper soil horizons, which corresponds to lower amplitudes of temperature and slower changes in water content compared to the shallow layers. The CO₂ concentration dynamics in shallow horizons is higher and faster. Rapid changes in soil CO₂ production may occur for example after a rain pulse. These changes are usually short-term but can be very intensive depending on rain pulse strength and dryness of the soil. Despite the temporariness, these pulses may play an important role in carbon budget in some ecosystems. This study assumed that Accurel tubes are a good tool for precise detection of such rapid responses in individual horizons. The profile measurements of soil CO₂ concentration can provide better description of the soil CO₂ production of rain events as to how fast is the onset? What is the course of the CO₂ concentration changes? Or what is the contribution of individual horizons?

It was found that equilibration of CO₂ concentration in the outer and inner space of the Accurel tube ranged between 29 and 71 s. This study results showed that this response was lower under low CO₂ concentration conditions and when the change of CO₂ concentration in the outer space was low. The CO₂ concentration in the soil can be several thousands, which supports fast response of CO₂ concentration change within the tube. Concerning the change of CO₂ concentration in the outer space, we do not expect such a high and fast increase as in our experiment. However, according to the equation (2), after an increase of CO₂ concentration in the outer space by 5 ppm would be just 64 s. This lag was assumed to be almost negligible and that the Accurel tubes are suitable for determination of the instantaneous CO₂ concentration and its changes in the soil, even though the lag in situ can be modified by actual soil conditions as the CO₂ diffusivity rate increases with temperature but decreases with soil water content.

Conclusions
This work analyzed the rate of the response of CO₂ concentration of the air within the polypropylene membrane tubes Accurel® PP V8/2 HF (often used for CO₂ concentration measurements in the soil) to changes in CO₂ concentration in their outer space. It was found that higher the CO₂ concentration and higher the change in CO₂ concentration in the outer space of the tubes, the faster was the change in CO₂ concentration within the tube. The best model for these relationships was hyperbola model and the corresponding equations of these models were determined. On the basis of these equations, the change by 5 ppm in the outer air CO₂ concentration results in 64 s time lag in equalization of CO₂ concentration in the tube on the actual level. On the base of our results, it is assumed that the tested membrane tubes are suitable for determination of the instantaneous CO₂ concentration and its rapid changes in the soil.

Acknowledgements
The authors give special thanks to the Ing. Stanislav Stellner for his technical cooperation in planning of experiment and during the actual experiment. The instruments used were supported by the Ministry of Education, Youth and Sports of CR within the National Sustainability Program I (NPU I), grant number LO1415, and by the project for national infrastructure support CzeCOS/ICOS Reg.No. LM2015061.

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