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# Temporal changes in soil pore space $CO_2$ concentration and storage under permanent grassland

C.R. Flechard *, A. Neftel, M. Jocher, C. Ammann, J. Leifeld, J. Fuhrer

*Agroscope Reckenholz-Tänikon, Research Station ART, Air Pollution/Climate Group, Reckenholzstrasse 191, 8046 Zürich, Switzerland*

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**Abstract**

Carbon dioxide concentrations were measured semi-continuously in soil pore space under permanent grassland for a 3-year period, using gas-permeable membrane tubes buried at various depths in the soil, in an attempt to quantify temporal variations of soil $CO_2$ storage. Diurnal wavelike variations in $CO_2$ concentration were observed systematically through the soil profile down to 50 cm, and the patterns and amplitude of mean diurnal waves depended on soil- and environmental conditions. For moderate to high soil water contents (SWC), soil $CO_2$ concentrations were positively correlated with soil temperature on a diurnal basis, resulting from an exponential increase of soil respiration with temperature and a shift in thermodynamic gaseous/aqueous phase equilibria. In dry conditions, however, air-filled porosity $CO_2$ concentrations tended to be lowest in the late afternoon and highest in the early morning, and thus negatively correlated with soil temperature. The storage of $CO_2$ in soil was calculated in the air-filled and in the water-filled pore fractions using Henry's law and carbonate chemistry. Storage estimates were extremely sensitive to soil pH and a parametrisation of soil pH as a function of soil water content was derived from field measurements and used in the storage calculation scheme. Instantaneous rates of soil $CO_2$ storage change with time were negatively correlated with atmospheric friction velocity in dry and moderately wet conditions, though in very wet conditions storage changes were dominated by vertical movements of soil water. The data suggest that $CO_2$ can accumulate in the soil during the night when transport is restricted to molecular diffusion through soil layers, and that wind-induced pressure pumping results in a gradual daytime flushing out. These findings may help account for the oft-reported $u_*$-dependence of night-time eddy covariance respiration fluxes.


*Keywords:* Carbon dioxide; Soil concentration; Ecosystem respiration; Storage change; Eddy correlation; Pressure pumping

## 1. Introduction

Atmospheric carbon dioxide ($CO_2$) is after water vapour the main greenhouse gas responsible for radiative forcing and climate change (Houghton et al., 2001). Terrestrial ecosystems have in the last decade of the twentieth century been suggested by inverse modelling studies to be potential sinks for $CO_2$ (Tans et al., 1990; Ciais et al., 1995; Denning et al., 1995), and several international integrated research programs and networks are currently aiming at a better understanding of the functioning of ecosystems and at the characterization and quantification of carbon sinks (Aubinet et al., 2000; Baldocchi et al., 2001; Valentini et al., 2000). Eddy covariance (EC) is now widely recognized and applied in flux monitoring networks across N. America and Europe as the standard measurement method for long-term studies of the net ecosystem exchange (NEE) of $CO_2$, upon which annual carbon budgets are established (Goulden et al., 1996).

* Corresponding author. Tel.: +41 44 377 75 11; fax: +41 44 377 72 01.
*E-mail address:* chris.flechard@art.admin.ch (C.R. Flechard).

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There remain however areas of uncertainties in the determination of long-term NEE using the EC technique, which are the focus of on-going investigations (*e.g.* Massman and Lee, 2002). In particular, the issue of the potential underestimation of the $CO_2$ efflux ($F$) in the night-time stably stratified surface layer, and its dependence on friction velocity ($u_*$) (Gu et al., 2005) have caused much debate. In many studies over forest in particular, it has been shown that the temperature-normalized, air column storage-corrected, night-time $CO_2$ efflux increases with $u_*$ (Goulden et al., 1996), sometimes linearly (Aubinet et al., 2000), sometimes levelling off after a given $u_*$ threshold (Pattey et al., 2002). It is commonly argued that the biological source strength (or ecosystem respiration, $R_{eco}$) is not a function of air movement (Wofsy et al., 1993; Goulden et al., 1996), and that there are a number of instrumental, methodological and micrometeorological reasons as to why fluxes could be underestimated by EC in conditions of suppressed turbulence (Massman and Lee, 2002). This line of thought implies that such fluxes should either be discarded or corrected up to the theoretical $R_{eco}$.

The soil/canopy ecosystem must be regarded as a transitory buffer zone for $CO_2$, whose biogenic production in that space must be seen as the sum of the exchange flux measured above the canopy and of storage ($Q$) change with time within the system ($R_{eco} = F + dQ/dt$). The fact that night-time micrometeorological measurements occasionally indicate a $CO_2$ flux lower than the estimated biological source strength may not necessarily constitute evidence for a flaw or bias in the measurements themselves if the system $CO_2$ storage change accounts for the discrepancy between $R_{eco}$ and $F$.

Crucially, the whole system $CO_2$ storage needs to be accurately quantified in order to establish whether ecosystem respiration is indeed balanced by the exchange flux and the instantaneous change in storage. The $u_*$-dependence of the temperature-normalized $CO_2$ efflux reported in the literature generally includes changes in $CO_2$ storage in the air column between ground level and sensor height ($dQ_{AC}/dt$), but storage in the other compartment of the ecosystem, namely the underlying soil ($Q_S$), has not been accounted for so far. Much of the research to date on $CO_2$ concentration in soil has focused on predicting the soil respiratory $CO_2$ efflux using diffusion models (Fang and Moncrieff, 1999) and/or measured vertical concentration profiles (DeJong and Schappert, 1972; Davidson and Trumbore, 1995; Risk et al., 2002; Tang et al., 2003; Jassal et al., 2005).

In this paper, we use continuous measurements of $CO_2$ in soil pore space to quantify soil $CO_2$ storage and assess the likely magnitude of temporal changes in this term, which are brought about by cyclical (diurnal) variations in temperature, moisture and other environmental parameters. We hypothesize that soil $CO_2$ storage changes may explain part of the "missing" night-time EC respiration flux, and that below-ground, in addition to above-ground, $CO_2$ storage should be considered. The results of a monitoring study over three years of soil $CO_2$ concentrations under grassland are shown, together with simulations of $CO_2$ storage in the gaseous and aqueous phases of soil pores. The data are then examined in the light of measured EC exchange flux data from the same site, within the framework of the CarboEurope IP flux network.

## 2. Materials and methods

### 2.1. The experimental site

Soil $CO_2$ concentrations and turbulent $CO_2$ exchange fluxes were measured at a grassland site in Oensingen, Central Switzerland (7°44′E, 47°17′N), at an altitude of 450 m amsl. The soil is stagnic cambisol (eutric), with pH around 7, a soil organic carbon (SOC) content of 27 mgC $g^{-1}$ soil dry matter in the layer 0–30 cm, and a C/N ratio of 9.6. The climate is temperate continental, with an average annual rainfall of about 1100 mm and a mean annual air temperature of 9 °C. The grass field received an annual nitrogen (N) fertilization in the order of 200 kg $ha^{-1}$, of which 75% in the form of cattle slurry in 1 or 2 applications in spring and summer, and the remaining 25% in the form of solid ammonium nitrate ($NH_4NO_3$) pellets typically in late spring and late summer. The field was converted from a long term arable rotation to permanent graminae-clover grassland in May 2001. There was no grazing and grass was mown typically 3–4 times yearly and harvested as hay or silage. More details on the timing of fertilizer application and cuts are provided in Flechard et al. (2005) and Ammann et al. (in press).

### 2.2. Soil gas concentration measurements

Carbon dioxide concentrations, expressed hereinafter as a mixing ratio $pCO_2$ (ppm), were measured from July 2002 to November 2005 in the air-filled porosity of soil at 5 depths down to 50 cm, using the MEmbrane Tube Technique (METT) (Gut et al., 1998). Membrane tubes are essentially hydrophobic, gas-permeable porous polypropylene tubes (Accurel® PP V8/2), with