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IMPORTANCE OF NON-DIFFUSIVE TRANSPORT FOR SOIL CO_2 EFFLUX IN A TEMPERATE MOUNTAIN GRASSLAND

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Abstract

Soil respiration and its biotic and abiotic drivers have been an important research topic in recent years. While the bulk of these efforts has focused on the emission of CO_2 from soils, the production and subsequent transport of CO_2 from soil to atmosphere received far less attention. However, to understand processes underlying emissions of CO_2 from terrestrial ecosystems, both processes need to be fully evaluated. In this study, we tested to what extent the transport of CO_2 in a grassland site in the Austrian Alps could be modelled based on the common assumption that diffusion is the main transport mechanism for trace gases in soils. Therefore, we compared the CO_2 efflux calculated from the soil CO_2 concentration gradient with the CO_2 efflux from chamber measurements. We used four commonly-used diffusion-driven models for the flux-gradient approach. Models generally underestimated the soil chamber effluxes and their amplitudes, indicating that processes other than diffusion were responsible for the transport of CO_2. We further observed that transport rates correlated well with irradiation and, below a soil moisture content of 33%, with wind speed. This suggests that mechanisms such as bulk soil air transport, due to pressure pumping or thermal expansion of soil air due to local surface heating, considerably influence soil CO_2 transport at this site. Our results suggest that non-diffusive transport may be an important mechanism influencing diel and day-to-day dynamics of soil CO_2 emissions, leading to a significant mismatch (10-87% depending on the model used) between the two approaches at short timescales.

1. Introduction

Soil CO_2 efflux is the largest source of CO_2 from terrestrial ecosystems; annually, approximately 98 Pg CO_2 is emitted from soils (Bond-Lamberty and Thomson, 2010). Although in recent years the number of studies on soil CO_2 fluxes has increased largely, and high frequency measurements have provided new insights in short-term dynamics of CO_2 efflux (see e.g., Vargas et al., 2011), the efflux of CO_2 from soil to atmosphere and its biotic and abiotic drivers remain an important topic of debate (e.g., Subke and Bahn, 2010). A major reason for this ambiguity is related to the fact that, in the short-term, soil CO_2 efflux does not equal soil CO_2 production (also termed soil respiration, the sum of microbial and root respiration). Our limited knowledge of the CO_2 transport through the soil restricts our understanding of the role of the various abiotic and biotic controls on soil respiration (Phillips et al., 2011; Subke and Bahn, 2010).

Most often, soil CO_2 efflux is measured using soil chambers, but since the early 2000s, solid-state CO_2 sensors that measure soil CO_2 concentrations at different soil depths are becoming more common. In contrast to soil chambers, solid-state CO_2 sensors allow continuous high frequency measurements of the CO_2 gradient with minimal disturbance of the natural conditions, such as, air pressure or wind velocity (Pingintha et al., 2010; Tang et al., 2003) and soil microclimate. For this reason, estimation of the soil CO_2 efflux from soil CO_2 concentrations, the so-called flux-gradient approach (or FGA), is rapidly gaining popularity (e.g., Hirano et al., 2003; Jassal et al., 2005; Jassal et al., 2004; Pumpanen et al., 2008; Tang et al., 2003; Tang et al., 2005; Turcu et al., 2005; Vargas and Allen, 2008a; Vargas and Allen, 2008b). This method uses Fick's law of diffusion (Eq. 1) to compute soil CO_2 efflux and thus implies the assumption that diffusion is the only transport mechanism for CO_2 through the

soil. Potential effects of, for example, air pressure differences (following advection or wind shear) are often neglected. Soil CO_2 efflux F is calculated via the flux-gradient method as:

$$F = -D_s \frac{\partial C}{\partial z} \quad \text{(Eq. 1);}$$

where D_s is the effective diffusion coefficient (see Materials and Methods for more detailed information) and C is the CO_2 concentration at depth z in the soil.

Gas diffusion in soils differs from that in free air, because solid and liquid obstacles reduce the cross-sectional area and increase the mean path length for the diffusing molecules (Sallam et al., 1984; Werner et al., 2004). Soil properties such as water content, texture and bulk density therefore determine the rate of diffusion (Moldrup et al., 1999; Pumpanen et al., 2003; Vargas et al., 2010). Reliable estimates for the diffusion coefficient are of critical importance when using Fick's law to estimate soil CO_2 efflux from soil CO_2 concentrations. Several commonly used models have been proposed to calculate the diffusion coefficient, all of them depending primarily on the air-filled pore space and thus varying inversely with soil water content (Jassal et al., 2005).

Generally it is assumed that, provided a good estimate of the diffusion coefficient is available, the soil CO_2 concentration gradient translates directly to soil CO_2 efflux. However, there is limited evidence that non-diffusive transport, such as pressure pumping (summarized in Takle et al., 2004) and advective transport due to heating of the soil surface (Ganot et al., 2014), may strongly influence soil CO_2 emissions at the timescale of seconds. Air pressure at the soil surface fluctuates whenever turbulent air moves over the surface and enhances the exchange of gases at shallow depths (Kimball and Lemon, 1971). This bulk air gas transport is increased with increasing permeability of the soil, corresponding to a decreasing soil water content, and by thermal advection. As the soil water content decreases, the air-filled porosity increases, enhancing both diffusive and non-diffusive transport.

While the potential relevance of non-diffusive transport has been addressed at a very short timescale mostly, it is important to test if it plays a role at half-hourly time steps, which is the highest time-resolution typically achieved in soil respiration studies. So far, few such studies have tested how well rates of chamber-measured soil CO_2 efflux and those estimated from the flux gradient approach compare across the season (Riveros-Iregui et al., 2008), when non-diffusive transport may intermittently decouple fluxes derived from these two approaches.

We aim to deduce the importance of non-diffusive transport for soil CO_2 effluxes by comparing two in-situ measurement methods (chamber and soil concentration gradient). Given that the CO_2 efflux is derived from the concentration gradient using diffusion models, the discrepancy between CO_2 effluxes from both measurements can be an indication for non-diffusive gas transport.

We tested the hypotheses that the role of non-diffusive transport (i.e. the mismatch between the two approaches) increases with increasing radiation and wind speed and with decreasing soil moisture.

2. Materials and methods

2. 1. Site description

The study was carried out in a mountain meadow at Kaserstattalm, Neustift, in the Austrian Central Alps (cf. Bahn et al., 2009). Mean annual temperature and precipitation are 3.0 °C and 1097 mm, respectively. The meadow is located at 1820 m asl and is fertilized with manure in spring, cut once in late July or early August and lightly grazed in September. The dominating plant species include the grasses *Anthoxanthum odoratum* L. and *Festuca rubra* L., and the forbs *Alchemilla vulgaris* L., *Leontodon hispidus* L. and *Trifolium repens* L. The soil is a cambisol on siliceous bedrock with a topsoil pH of 5.5. The soil texture is 43% sand, 47% silt and 11%

clay, the bulk density is 860 kg m^{-3}. The meadow is characterized by a comparatively high productivity and high soil respiration rates, typical for non water-limited Central European mountain meadows (Bahn et al., 2010; Schmitt et al., 2010).

2. 2. Measurements

Soil CO_2 concentration measurements were made during the growing season of 2009 using Vaisala CARBOCAP solid-state CO_2 sensors (model GMT 221, Vaisala, Helsinki, Finland) at depths of 10 and 5 cm and the Li-8150 system (Li-Cor, Lincoln, NE, USA) at 0 cm. At the same depths, soil temperature (averaging soil thermocouple probe TCAV; Campbell Scientific) and moisture (ML2x; Delta-T Devices, Cambridge, UK) were measured, and incident photosynthetically active radiation (PAR) (BF2H; Delta-T Devices) was measured above the canopy at 2m height. Continuous recordings at 0.05 Hz were averaged and half-hourly values recorded using an automated station (CR10X; Campbell Scientific). Values of soil CO_2 concentration were corrected for temperature and pressure using the ideal gas law according to the manufacturer (Vaisala, Helsinki, Finland). Soil CO_2 efflux at the soil surface was measured using an automated soil respiration system (Li-8100 and Li-8150; Li-Cor, Lincoln, NE, USA) over measurement intervals of 2 minutes. The chambers were white to minimize heating. Possible pressure changes due to a Venturi effect are largely eliminated by the design of the vent used with the chamber (Xu et al., 2006).

2. 3. CO_2 diffusion through the soil

2.3.1 Effective diffusivity

Using Fick's law (Eq. 1) to calculate soil CO_2 efflux from the soil CO_2 concentration gradient requires good estimates of the diffusion coefficient D_s ($m^2\ s^{-1}$), also named effective diffusivity. D_s can be estimated as

$$D_s = D_a \xi \qquad \text{(Eq. 2);}$$

where D_a ($m^2\ s^{-1}$) is the CO_2 diffusion coefficient in free air and ξ ($m^3\ m^{-3}$) is the so-called tortuosity factor, the product of the air-filled porosity ε_a and the tortuosity τ (Jassal et al., 2005; Jury et al., 1991). It accounts for the increase in path length and decrease in cross-sectional area in soils.

The variation of D_a with temperature and pressure is given by

$$D_a = D_{a0} \left(\frac{T}{T_0}\right)^{1.75} \left(\frac{P}{P_0}\right) \qquad \text{(Eq. 3);}$$

with T the temperature (K), P the air pressure (Pa) and D_{a0} a reference value at T_0 (293.15 K) and P_0 (1.013×10^5 Pa), given as $1.47 \times 10^{-5}\ m^2 s^{-1}$ (Jones, 1992).

The air-filled pore space ε_a ($m^3\ m^{-3}$) is defined as the difference between total porosity ϕ and the volumetric water content θ ($m^3\ m^{-3}$) of the soil.

$$\varepsilon_a = \phi - \theta \qquad \text{(Eq. 4).}$$

Several relationships between ξ and ε_a have been proposed to determine the adjustment factor ξ. Here we compare four of the most commonly used models.

$$\xi = 0.66\varepsilon_a \qquad \text{(Penman, 1940) (Eq. 5)}$$

$$\xi = {\varepsilon_a}^{1.5} \qquad \text{(Marshall, 1959) (Eq. 6)}$$

$$\xi = \frac{{\varepsilon_a}^{10/3}}{\phi^2} \qquad \text{(Millington and Quirk, 1961) (Eq. 7)}$$

$$\xi = \phi^2 \left(\frac{\varepsilon_a}{\phi}\right)^{\beta S} \qquad \text{(Moldrup et al., 1999) (Eq. 8)}$$

In Eq. 8, S is the percentage of mineral soil with particle size > 2 µm (S = 0.8 for our study site) and β is a constant equal to 2.9. Total porosity at the site is 0.57 m^3 m^{-3}. Note that in all four models, the air-filled pore space and thus total porosity, is a key factor determining the calculated efflux. Measurements of porosity on soil cores are often subject to uncertainties, especially on heterogeneous soils, and 10% uncertainty in estimated porosity translates into 27-80% uncertainty in calculated efflux (depending on the model used). For this uncertainty, corresponding to a porosity range of 0.51 to 0.63 m^3m^{-3} at our study site, the Millington and Quirk (1961) model is the most sensitive (up to 80% uncertainty on the efflux), while the Penman (1940) model is the least sensitive (27% uncertainty on the efflux).

2.3.2 Apparent diffusivity, D_{app}

The combination of chamber measurements and solid-state sensors allows calculation of the diffusion coefficient solely from measurements. To make a distinction with the effective diffusivities D_S calculated from Eqs. 5-8, we refer to the empirically obtained diffusivity coefficient as "apparent diffusivity, D_{app}". To calculate this, we used the difference between the CO_2 concentration measurements at 5 and 0 cm depth, which should capture the most productive zone of the grassland rhizosphere. When calculating D_{app} from Fick's law (Eq. 1), it is necessary to account for the temperature gradient in the soil, that causes changes in the soil air density and thus in the absolute gas concentration (Kowalski and Argueso, 2011). When this concentration gradient is proportional to the gradient in air density, it will not result in diffusional transport and yield wrong fluxes. Therefore we expressed CO_2 concentration as a molar fraction and accounted for the air density.

$$F = -\rho D_s \frac{\partial C}{\partial z} \quad \text{(Eq. 9);}$$

where F is the mass flux (kg m^{-2} s^{-1}), ρ is the density of air (kg m^{-3}) C is the relative CO_2 concentration (dimensionless) at depth z (m) in the soil.

$\mathrm{D}_{\mathrm{app}}$ can then be calculated by rearranging this equation:

$$D_{app} = -F_{ch}\frac{\partial z}{\rho \partial C} \text{ (Eq. 10);}$$

It is important to note that if the chamber soil CO_2 efflux results from transport mechanisms other than diffusion, these are also comprised by D_{app}.

3. Results

3.1 Measurements of soil CO_2 concentrations and soil CO_2 efflux

Chamber-based measurements of soil CO_2 efflux showed most variability at daily timescales, with an amplitude apparently in phase with variations in temperature, light (PAR) and wind speed (Fig. 1). Soil CO_2 concentrations measured with solid state sensors at 5 cm and 10 cm depth and measured with the Li-8150 system at 0 cm depth, were much less variable, both at seasonal and daily timescales. As the CO_2 gradient is a driver of the CO_2 efflux, we expected a clear relationship between the two types of measurements, but we found that the soil CO_2 concentration gradients from 5 to 0 cm and from 10 to 5 cm depth were uncoupled from the efflux measured with the chambers. Slopes of the correlations between the concentration measurements at 10 cm and at 5 cm depth with the fluxes, were not significantly different from zero (p=0.92 and p=0.33 respectively).

3.2 Calculation of soil CO_2 efflux with flux-gradient approach

Using Fick's law (Eq. 1), we calculated the soil CO_2 efflux from the measured soil CO_2 concentrations at 5 and 0 cm depth and the modeled diffusivity. We will refer to this calculated flux as the solid-state CO_2 efflux, as distinct from the chamber CO_2 efflux. Note that

we did not use the concentrations at 10 cm depth in this analysis, as the peak rhizosphere activity is assumed to be in the upper 5 cm of the soil. The four different models (see Eq. 5-8) to estimate the effective diffusivity, D_s, revealed large differences in estimated soil CO_2 efflux. Using the Penman (1940) and Marshall (1959) models for D_s yielded flux estimates within the range of the chamber measured fluxes, while the Moldrup et al. (1999) and Millington and Quirk (1961) models for D_s were both considerably lower than the chamber CO_2 effluxes (Fig. 2). Importantly, none of the four models was able to reproduce the large daily variation in soil CO_2 efflux that was observed with the chamber-based measurements (Fig. 2).

The diurnal course of the solid-state fluxes clearly followed that of the CO_2 concentrations, soil temperature and soil moisture content, while the course of the chamber fluxes followed that of wind speed and PAR. As a result, the daily peaks of solid-state fluxes lagged the chamber fluxes with approximately 4 hours.

3.3 Effective and apparent diffusivity, D_s and D_{app}

By inverting Fick's law and combining the chamber-based CO_2 efflux measurements and the solid-state CO_2 concentration measurements, we calculated D_{app} and compared this with the four commonly used models to calculate D_s. D_s calculated from all four models differed strongly from D_{app} (Fig. 3a). While D_s decreases linearly with increasing soil moisture, D_{app} revealed a different pattern (Fig. 3a). Only for soil water contents above 33%, D_{app} decreased markedly with increasing soil moisture. At soil water contents below 33%, D_{app} was unrelated to soil moisture and varied substantially even at similar values of soil water content.

Because soil moisture is the primary determinant of gas diffusion in soils (see Eq. 4-8), the high variation of D_{app} at similar soil moisture, especially at soil moisture levels below 33%, suggests that processes other than diffusion influence the transport of CO_2 from soil to

207 atmosphere. Therefore, we tested whether light (PAR), soil temperature and wind speed
208 affected D_{app}. Fig. 3b and 3c show that D_{app} indeed responded positively to variations in light
209 and wind speed. We found no correlation between the soil temperature and D_{app} and also the
210 temperature dependence of D_s was very weak (data not shown). We further explored the
211 correlations of D_{app} with light and wind speed by fitting for each day the 48 half-hourly values
212 of D_{app} versus PAR and wind speed. The correlation of D_{app} and wind speed was consistently
213 positive for days with relatively low soil water content (<33%; Fig. 4a, asterisks). Correlations
214 between D_{app} and PAR were positive for almost all days (Fig. 4b), indicating that D_{app} and thus
215 the rate of CO_2 transport, increases with higher irradiation. Furthermore, the slopes of the
216 24-hour fits of D_{app} versus PAR were positively correlated with wind speed (Fig. 4c), indicating
217 that the coupling of D_{app} and irradiation is amplified under windy conditions. To rule out any
218 bias in either of our field measurement series, we subjected other datasets of combined solid-
219 state and chamber measurements, from the previous year and with different placement, to
220 this analysis and found similar results (data not shown).
221 We tested how much of the overall variation in D_{app} could be attributed to variation in PAR,
222 wind speed and soil moisture, both for days above and below the threshold of 33% soil
223 moisture content. The results of these multiple linear regressions are summarized in Table 1.
224 For the entire dataset, the combination of the three parameters explained 67% of the
225 variation in D_{app}. The combination of wind speed and PAR explained a larger part of the
226 variation in D_{app} under moderately wet conditions (47%) than under very wet conditions
227 (40%).
228 Comparing half-hourly values of soil CO_2 concentrations with soil CO_2 efflux measured once
229 every half hour, implies comparing different integration times. To avoid statistical bias related
230 to a reduction in variability due to longer integration time, we tested how the soil CO_2 efflux

231 depended on the integration time of the flux-gradient approach. To this end, we used the
232 Penman (1940) equation, because it yielded the best result in predicting the effective
233 diffusivity in the soil (see Fig. 2). Increasing the integration time of the solid state and chamber
234 measurements resulted in slightly improving accordance between D_{app} and D_s (Fig. 5), but
235 even increasing the integration time to one month yielded poor agreement between D_{app} and
236 D_s.
237
238 **4. Discussion**
239 Soil CO_2 concentrations and effluxes were studied at a mountain meadow in the Stubai valley
240 (Austrian Alps) during the period of peak biomass production in 2009. Diurnal variations in
241 concentrations were small, while they were much larger for the chamber measurements,
242 exceeding even the seasonal variability. Furthermore, when pooling all data pairs, both types
243 of measurements seemed largely uncoupled, which is surprising given that the concentration
244 difference of CO_2 between soil and atmosphere is assumed to be the main driver of the soil
245 CO_2 efflux. Part of this uncoupling might be attributable to a time lag between photosynthesis
246 and CO_2 efflux, as reported by Vargas et al. (2011), but since such lag was not observed in the
247 times series of soil CO_2 concentration and efflux (Fig. 1), we expect it to play a minor role here.
248 The importance of a storage term was evaluated by looking at the instantaneous changes in
249 soil CO_2 concentrations, but as these turned out to be very small, a storage flux is unlikely to
250 explain the uncoupling of concentration and flux measurements here. Flechard et al. (2007)
251 pointed out that storage occurs only when diffusive transport prevails.
252 To evaluate the importance of non-diffusive transport mechanisms in determining the soil
253 CO_2 efflux at this site, we compared solid-state CO_2 fluxes, calculated with the flux-gradient
254 approach, to the chamber CO_2 fluxes. The use of Fick's law in the flux-gradient approach

255 requires estimates of soil diffusivity that are in turn determined by the tortuosity factor.
256 Different models exist for calculation of this tortuosity factor, all of them depending strongly
257 on the air-filled pore space and thus on the soil water content (Werner et al., 2004). Among
258 the models tested here, the Penman (1940) and Marshall (1959) models performed better
259 with respect to the overall magnitude of the flux, the Penman model also being the least
260 sensitive to uncertainties in porosity estimates. The Penman model yielded the highest soil
261 CO_2 effluxes, which, in contrast to what has been frequently reported (Pingintha et al., 2010;
262 Sallam et al., 1984; Werner et al., 2004), did not exceed chamber fluxes, but predicted fluxes
263 within the same range. The other three models resulted in fluxes (much) lower than those
264 from chamber measurements. This was especially the case for the Moldrup et al. (1999) and
265 Millington and Quirk (1961) model, although these have often been reported as yielding the
266 best results (Pingintha et al., 2010; Sallam et al., 1984; Werner et al., 2004). In our study, the
267 most important outcome was that none of these diffusivity models was able to predict the
268 short term (i.e. diel and day to day) variation of the soil CO_2 efflux in an acceptable way (Fig.
269 2).
270 Further analyses pointed out that this disagreement is related to the fact that the tortuosity
271 models, based on diffusive transport, depend almost completely on the soil water content.
272 The role of the moisture content on diffusive transport is twofold. First, by decreasing the air-
273 filled pore space, as diffusion of CO_2 through water is much slower than diffusion through air.
274 Second, there can be a hysteric effect of the water content on the effective diffusivity, D_s
275 being higher at a similar water content during wetting than during drying (Goffin et al., 2014;
276 Rouf et al., 2012). It is important to note here that also the short-term response of soil
277 respiration to changes in soil moisture is not monotonic; CO_2 production increases from low

278 to intermediate soil moisture, reaches a plateau at optimum moisture, and decreases again
279 at high soil moisture (Vicca et al., 2014).
280 At our site, however, the rate of CO_2 transport from soil to atmosphere depended not only
281 on soil moisture, but also on irradiation (PAR) and wind speed. Correlation coefficients of the
282 fits of apparent diffusivity, D_{app}, versus wind speed were consistently positive on days that
283 were not very wet, i.e. when soil water content was below 33% (Fig. 4a). D_{app} was also
284 positively related to PAR (Fig. 4b), indicating a positive light effect on CO_2 transport from soil
285 to atmosphere. Last, the slopes of the linear regressions showed that the coupling of D_{app} and
286 PAR became stronger as wind speed increased (Fig. 4c). Note that higher values of PAR and
287 wind speed were recorded in periods when soil moisture content was below 33%, therefore
288 leading also to higher values of D_{app} in these periods. The response of D_{app} to these drivers,
289 on the other hand, did not differ for periods with soil moisture content above and below 33%
290 (intercepts of the correlations differed but not the slopes). The effect of wind speed on D_{app}
291 was similar during day and night time.
292 The large diel variations we observed in D_{app} and its tight coupling to PAR, should not be
293 mistaken for a soil respiration-driven effect on diffusive CO_2 transport. Soil respiration is
294 known to be strongly influenced by temperature and thus exhibits a pronounced diel pattern.
295 This diel pattern can be further amplified by the linkage between belowground carbon
296 allocation and photosynthetic activity. The increase in photoassimilates allocated
297 belowground was often shown to stimulate autotrophic and heterotrophic respiration (Bahn
298 et al., 2009; Hogberg et al., 2001; Janssens et al., 2001; Kuzyakov, 2006; Kuzyakov and
299 Gavrichkova, 2010).
300 The diurnal pattern in soil respiration was clearly seen in the chamber-based soil CO_2 efflux
301 measurements, but surprisingly much less in the soil CO_2 concentration measurements. This

302 suggests that an increased transport rate, exceeding diffusion, during the day must have
303 prevented soil CO_2 concentrations to rise, while soil respiration did increase. Diffusion
304 depends primarily on soil moisture and on the concentration gradient, both of which varied
305 only little during the day. Enhanced transport of CO_2 through the soil, via other processes
306 should thus explain the discrepancy between the large diel amplitude of soil CO_2 efflux and
307 the relatively steady soil CO_2 concentrations.
308 Several mechanisms causing bulk flow of CO_2-enriched soil air have been described in
309 literature (see Kuang et al. (2013) for an extensive review) and can occur in all soils when
310 pores are connected and not blocked by water (Cuezva et al., 2011). An increasing number of
311 authors have demonstrated a positive correlation between pressure pumping and soil CO_2
312 efflux (Arneth et al., 1998; Baldocchi and Meyers, 1991; Lewicki et al., 2010; Subke et al.,
313 2003). Takle et al. (2004) found that these pressure fluctuations penetrated into a dry soil up
314 to 50 cm with little attenuation and Bowling and Massman (2011) found a temporarily
315 transport enhancement through a forest snowpack up to 40% higher than diffusion. Pressure
316 pumping is controlled by the degree of permeability of the medium and the direction and
317 magnitude of the pressure gradient (Massman et al., 1995; Takle et al., 2003). Pressure
318 gradients can be caused by barometric waves, passage of synoptic weather systems, short-
319 period atmospheric turbulence and wind blowing across irregular topography (Elberling et al.,
320 1998; Massman et al., 1997; Takle et al., 2004).
321 Bulk air transport (in this context called ventilation) was described in permeable, dry and
322 fractured media such as karst systems, and was found to be coupled to pressure gradients as
323 well as wind (Rey et al., 2012; Sanchez-Canete et al., 2013; Serrano-Ortiz et al., 2010).
324 The bulk exchange of gases is enhanced when drying of the soil increases the air-filled porosity
325 and by high wind speeds (Hirsch et al., 2004; Kimball and Lemon, 1971; Maier and Schack-

326 Kirchner, 2014; Sanchez-Canete et al., 2013; Subke et al., 2003). The positive correlation that
327 we found between D_{app} and wind under relatively dry conditions, could therefore be
328 attributable to pressure changes caused by wind shear at the soil surface.
329 Advective bulk air transport can also be triggered by the local heating of the soil surface
330 (Ganot et al., 2014). This heating would not be recorded by the soil temperature sensors,
331 which were installed at 5 and 10 cm depth, but inevitably coincides with measurements of
332 irradiation. A second light-coupled process that may amplify bulk soil air transport is the
333 breaking of the soil boundary layer following thermal expansion and uplifting of the air at the
334 soil-atmosphere interface.
335 Several things could improve the ability to accurately estimate CO_2 efflux from vertical
336 concentration gradients. First, D_s, and thus porosity and tortuosity, should be estimated
337 independently, using intact soil cores (DeSutter et al., 2008; Jassal et al., 2005) or in situ field
338 methods based on inert tracers such as radon (Risk et al., 2008), although even these methods
339 cannot fully capture the spatial and temporal dynamics of the soil gas diffusivity (Maier and
340 Schack-Kirchner, 2014). Next, part of the discrepancy that we observed between solid-state
341 and chamber CO_2 efflux, might be reconciled when both types of measurements are carried
342 out with the exact same measuring frequency and interval, as the variability of solid-state
343 concentrations with longer integration time will typically be lower otherwise. This was also
344 brought up by Riveros-Iregui et al. (2008), stating that solid-state sensors might not capture
345 rapid changes in soil properties and respiration, e.g. due to rainfall events. Several authors
346 state that the efflux rates calculated from concentration gradients might be unsuited for
347 deriving short-term fluxes, but that they could be useful for flux estimates over longer time
348 periods (eg. Vargas et al., 2010), when the importance of non-diffusive transport decreases.
349 However, even after integration over one month, we found that apparent diffusivity was

higher than effective diffusivity (Fig. 5), thus still resulting in an underestimation of soil respiration rates by the flux-gradient approach. Substantial uncertainty may furthermore arise from the assumption of a linear CO_2 concentration gradient in the soil (Maier and Schack-Kirchner, 2014), although Monson et al. (2006) found it a minor source of error compared to the estimations of D_s. The exact measurement height of the 0 cm concentration holds a negligible error, given that the magnitude and diel variability of soil CO_2 above the surface is small due to the atmospheric buffer and affects the gradient only very little (Riveros-Iregui et al., 2008; and own analysis).

Several previous studies did find good agreements between solid-state CO_2 efflux and chamber CO_2 efflux (Jassal et al., 2005; Liang et al., 2004; Pumpanen et al., 2008; Tang et al., 2005). These studies were conducted in dense forests where, in contrast to grasslands, both light and wind have difficulty penetrating into layers close to the soil surface. This is probably why their effect on soil gas transport was insignificant. Under such diffusion-dominated conditions, the flux-gradient approach can be successfully applied to predict the soil CO_2 efflux.

5. Conclusions and recommendations

Over the last decade, research in this field has focused on the measurement of fluxes at the soil surface using a variety of chambers and micrometeorological methods. Recently the flux-gradient approach proved to be a very cost-efficient way to calculate the soil CO_2 efflux that minimizes soil surface perturbations and provides insights into subsurface CO_2 dynamics. This method uses estimates for effective diffusivity, derived from different models primarily based on the air-filled pore space. Testing four commonly used models, we found substantial

deviation between observed and modeled diffusivity, leading to poor predictions of the soil CO_2 efflux when using the flux-gradient approach at shorter timescales.

Gaseous diffusion is often considered as the only mechanism for CO_2 to move from the soil to the atmosphere, while in reality several gas transport mechanisms can be distinguished in unsaturated porous media like soils, e.g. advective mass transport and pressure pumping. We found strong evidence for such non-diffusive CO_2 transport at our site, given that the rate of transport was coupled to irradiation, with an even stronger coupling under increasing wind speed. Wind speed also had a direct positive effect on the efflux rate when the soil moisture content comparatively low (< 33%), resulting in higher air-filled porosity.

Considering the importance of alternative transport processes is a prerequisite when using solid-state CO_2 concentration measurements to estimate soil CO_2 efflux at any given site. Deviation between apparent (data-based) and effective (model-based) diffusivity may be a first indication of non-diffusive gas transport. Apparent diffusivity can be evaluated by calculation from combined chamber and solid-state sensor measurements (as demonstrated here) or by direct in situ soil gas diffusivity measurements (e.g. with natural or injected ^{222}Radon as done by Risk et al. (2008)).

Given that non-diffusive transport is especially important at very short timescales and its influence decreases with increasing timescale, we recommend that future studies further explore the importance of the timescale considered (high-frequency versus low-frequency data) and the effects of uncertainties in porosity on this. Combined high-frequency measurements of soil CO_2 concentrations and its potential physical drivers, including air pressure and friction velocity, under a wider range of soil moisture conditions, are needed to obtain a more detailed picture of the mechanisms and timescales relevant for non-diffusive transport of CO_2 on soils.

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Figure legends

Figure 1:

Time series from May 28 until August 4 2009 of half hourly measurements of (a) soil CO_2 concentrations at 0, 5 and 10 cm depth, (b) soil CO_2 efflux from automated chambers, (c) photosynthetically active radiation (PAR), (d) soil temperature at 5 and 10 cm depth, (e) soil water content and rainfall and (f) wind speed on a mountain meadow at Kaserstattalm, Neustift, Austria.

Figure 2:

Comparison of measured and modeled soil CO_2 effluxes. The black line shows the soil CO_2 efflux measured by the soil chambers, the colored lines are the effluxes calculated using four different models: Pm: Penman (1940), MQ: Millington and Quirk (1961), Md: Moldrup et al. (1999), Ma: Marshall (1959).

Figure 3:

(a) Apparent diffusivity (D_{app}, black dots) and modeled diffusivity (D_s, colored dots) as a function of the soil water content (SWC) at 5 cm depth. The green lines are the regression lines of D_{app} versus SWC<33% ($y=-0.06x+5.66$, $R^2=0.02$, $p<0.01$) and D_{app} versus SWC>33% ($y=-0.45x+18.06$, $R^2=0.30$, $p<0.01$).

(b) D_{app} as a function of photosynthetically active radiation (PAR). The green line is the regression line ($y=0.002x+1.81$, $R^2=0.35$, $p<0.01$).

(c) D_{app} as a function of wind speed. The green line is the regression line ($y=0.66x+1.46$, $R^2=0.10$, $p<0.01$).

Figure 4:

(a) Correlation coefficients of 24-hour fits (using 48 half-hourly values for each fit) of apparent diffusivity (D_{app}) and wind speed. Open circles are days with soil water content below 33%, full circles are days with soil water content above 33%.

(b) Correlation coefficients of 24-hour fits of D_{app} and of photosynthetically active radiation (PAR).

(c) Slopes of 24-hour fits of D_{app} and PAR plotted against wind speed. The black line is the regression line ($y=0.19x+0.02$, $R^2=0.15$, $p<0.01$).

Figure 5:

The accordance between D_s (using the Penman 1940 model) and D_{app}, with increasing integration times of solid state and chamber measurements: 2 hours, 8 hours, 24 hours, 1 week and 1 month.

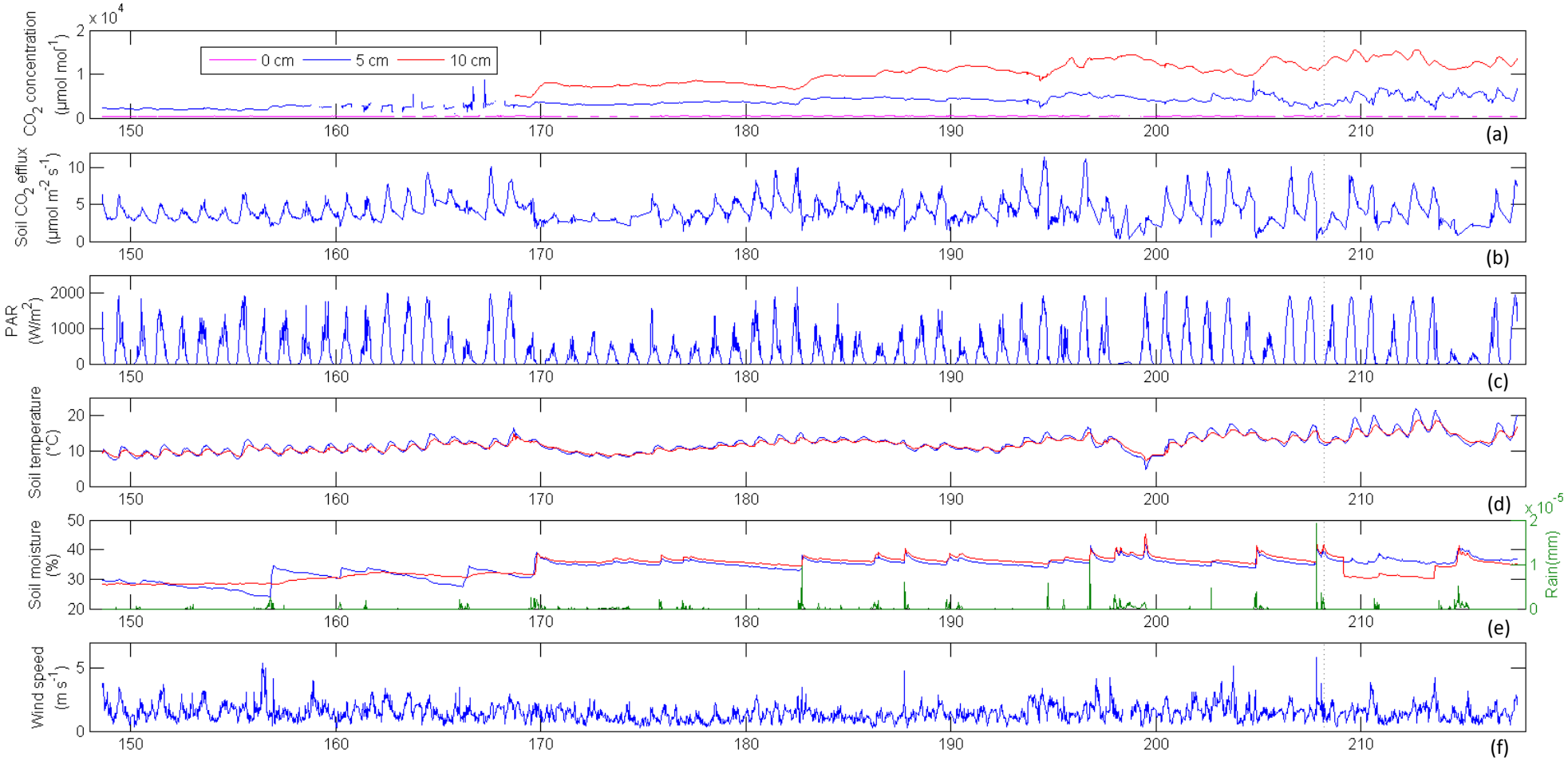
x 10^4
CO2 concentration (µmol mol-1)
0 cm
5 cm
10 cm
(a)
Soil CO2 efflux (µmol m-2 s-1)
(b)
PAR (W/m2)
(c)
Soil temperature (°C)
(d)
Soil moisture (%)
x 10-5
Rain(mm)
(e)
Wind speed (m s-1)
(f)
150
160
170
180
190
200
210

Figure 1

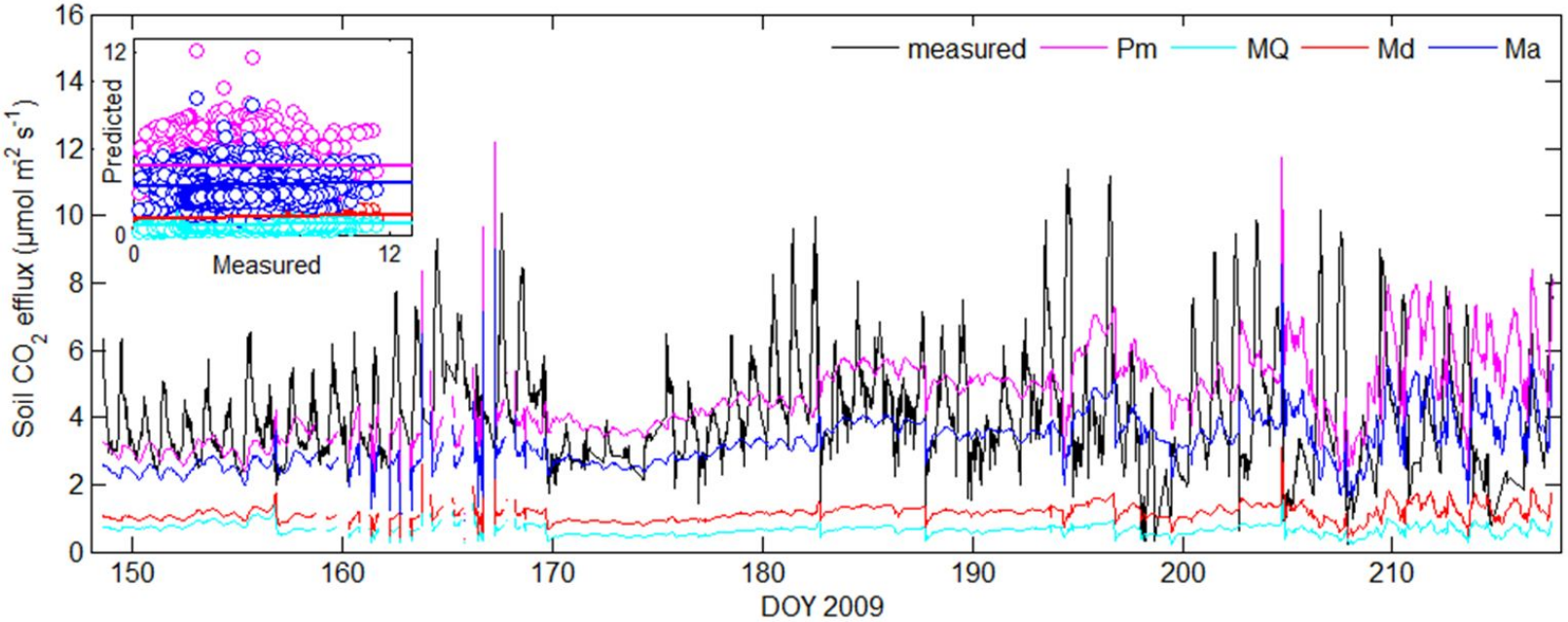
measured
Pm
MQ
Md
Ma
Soil CO_2 efflux (µmol m^2 s^{-1})
DOY 2009
Predicted
Measured
0
2
4
6
8
10
12
14
16
150
160
170
180
190
200
210

Figure 2

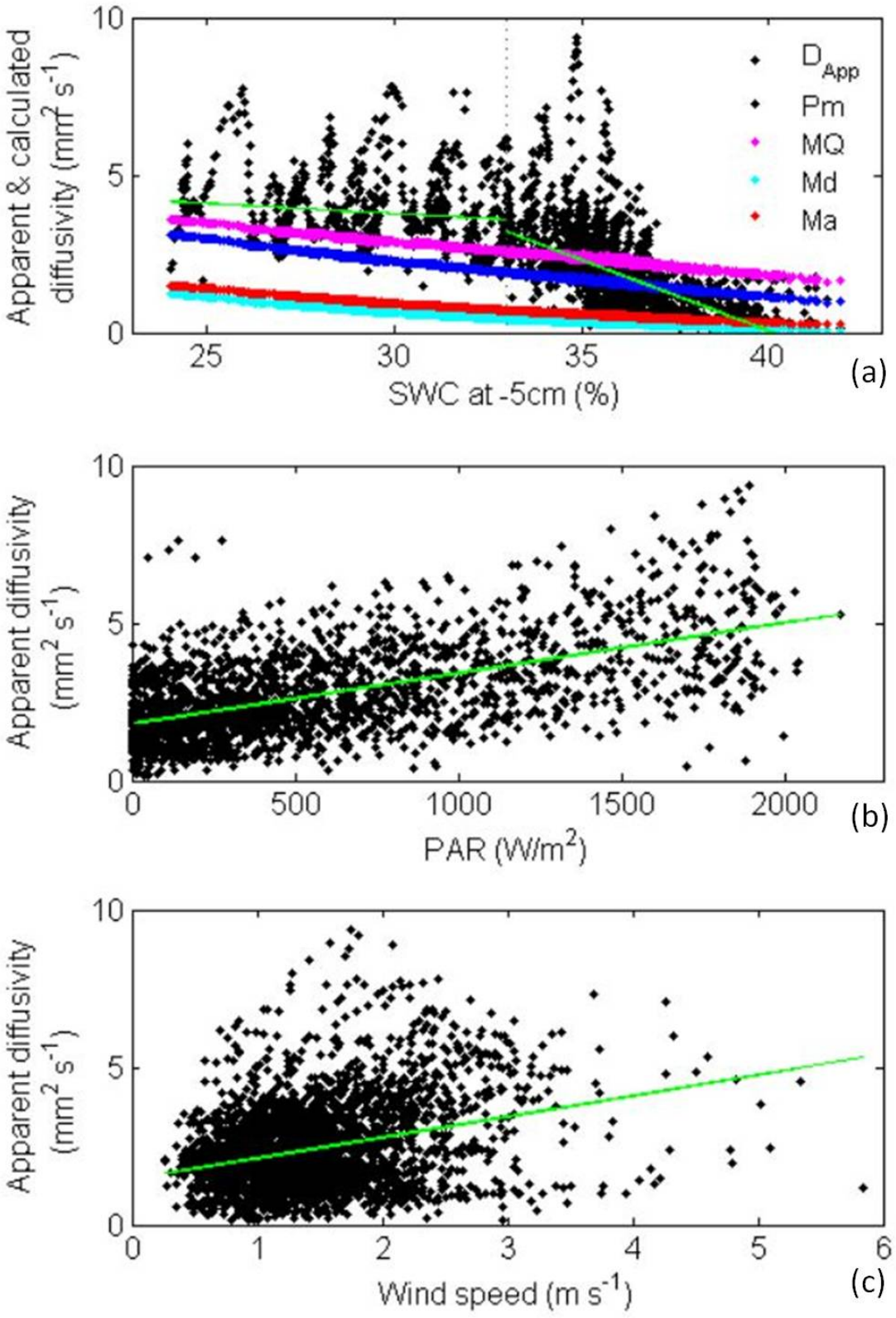
Apparent & calculated diffusivity (mm² s⁻¹)
10
5
0
25
30
35
40
SWC at -5cm (%)
D App
Pm
MQ
Md
Ma
(a)
Apparent diffusivity (mm² s⁻¹)
10
5
0
0
500
1000
1500
2000
PAR (W/m²)
(b)
Apparent diffusivity (mm² s⁻¹)
10
5
0
0
1
2
3
4
5
6
Wind speed (m s⁻¹)
(c)

Figure 3

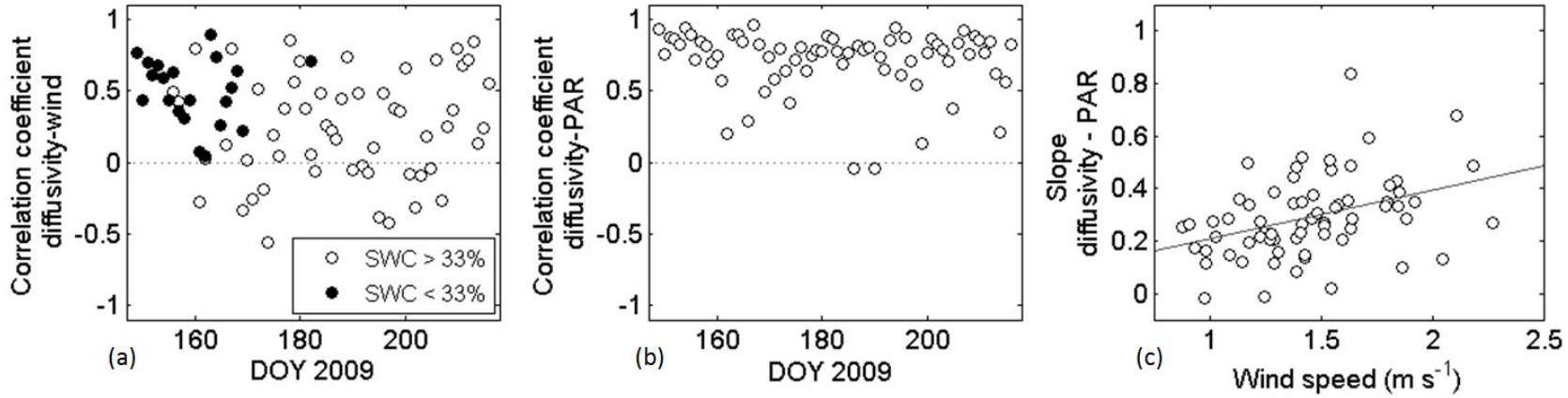
Correlation coefficient diffusivity-wind
SWC > 33%
SWC < 33%
(a)
DOY 2009
Correlation coefficient diffusivity-PAR
(b)
DOY 2009
Slope diffusivity - PAR
(c)
Wind speed (m s-1)

Figure 4

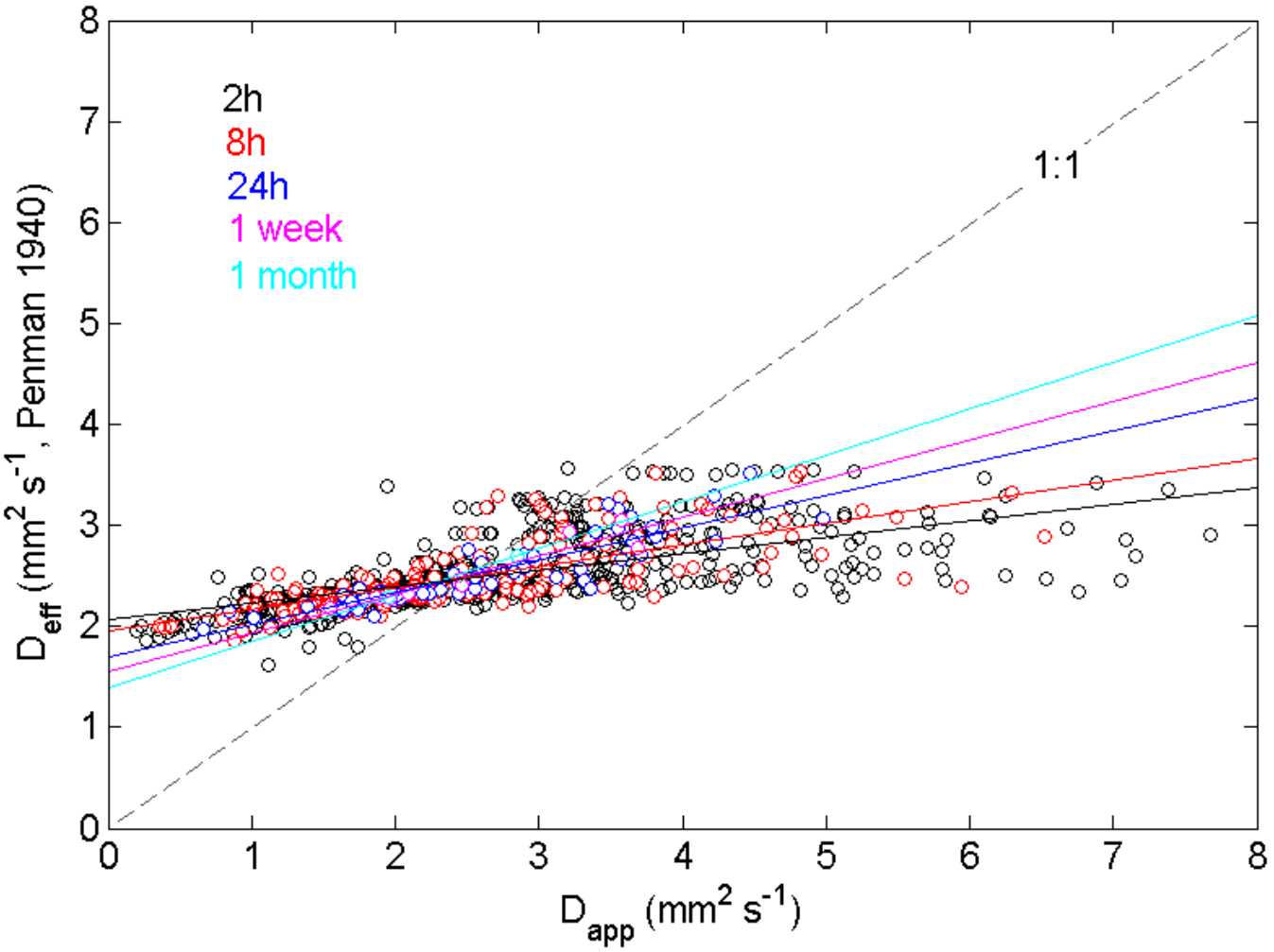
2h
8h
24h
1 week
1 month
1:1
D_{eff} (mm^2 s^{-1}, Penman 1940)
D_{app} (mm^2 s^{-1})
0
1
2
3
4
5
6
7
8

Figure 5

Table 1

Included parameters	% Variance in D_{app} explained		
	All data	SWC<33%	SWC>33%
Wind, PAR, SWC	67	57	61
Wind, PAR	36	47	40

Table 1:

Multiple linear regression of wind speed, photosynthetically active radiation (PAR) and soil moisture content (SWC) with apparent diffusivity (D_{app}), was used to calculate the percentage of variance in D_{app} explained by combinations of these three drivers. Regressions were carried out on the whole dataset, on the subset of data were SWC was below the threshold of 33% and on the subset of data were SWC was above this threshold.