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Assessing soil respiration in the soil profile

A study case of gradient-based CO₂ efflux and subsurface
production rates using soil diffusion chambers

PhD thesis

2009

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Summary

The impact of global warming on soil respiration is strongly related to the characteristics of deep-soil carbon and may differ with soil depth. Environmental parameters can affect the rates of soil CO₂ respiration not only temporally at daily and seasonal scale, but also spatially in vertical and horizontal dimensions. Therefore, it is important to evaluate soil subsurface CO₂ production and investigate the seasonal response of deep-soil respiration to different environmental conditions. In this respect, accurate techniques used to monitor the soil CO₂ concentrations in the soil profile offer the opportunity to identify localized sources and potential sinks in the soil, and to understand the processes that control CO₂ production and emission.

In this study, we developed an automated method to semi-continuously monitor soil CO₂ concentration in the soil profile, by using a new type of soil diffusion chamber. Their development aimed to combine the advantages of some of the methods developed by previous soil profile gradient studies, and to overcome some of their disadvantages. By using the high temporal resolution CO₂ concentrations profile, soil temperature, soil water content, and soil physical characteristics measurements from soil surface to 80 cm depth, we assessed the CO₂ concentration gradient and the soil diffusivity by using the Millington-Quirk model. Efflux calculated from soil CO₂ concentration gradient closely agreed with surface chamber efflux measurements, highlighting the accuracy of automated diffusion chamber on measuring CO₂ concentration not only at soil surface, but also within the soil profile. With the start of the growing season the CO₂ efflux showed an apparent differential response to soil warming and cooling which led to a

pronounced diurnal hysteresis effect. Furthermore, a phase shift between the daily peaks of CO₂ efflux and soil temperature increased during the growing season reaching a maximum time lag of approximately three hours in June. The soil respiration-temperature relationship described by Q_{10} varied from 4.3 to 7.6 throughout the soil profile, showing better R^2 values when soil temperature measured between 10 and 40 cm depth was considered.

Partitioning the soil profile in four layers we assessed the CO₂ production rates within each layer. Over four seasons in 2008 the top layer (0-10 cm) contributed on average 59% of total soil CO₂ efflux, the 10-20 cm layer 35%, the 20-40 cm layer 6%, whereas the bottom layer (40-80 cm) had a negligible contribution. The trends of the surface CO₂ efflux more closely followed changes of CO₂ production in the top 20 cm of the soil profile. Considering the mean annual C of aboveground biomass residues falling to the ground (2.9 gC m⁻² day⁻¹), depending on the climatic conditions the top layer of the soil profile represented a significant transient source or sink of carbon on a seasonal basis.

The results of this study suggest that the use of techniques such as soil diffusion chambers, which permit continuous and precise measurements of soil CO₂ concentration, combined with continuous stable carbon isotope analysis of the respired CO₂, would clearly be an advantage to explore the fate of the soil carbon into specific biological soil components. Moreover, the use of soil diffusion chambers would provide important additional information on soil profile CO₂ storage to improve the estimation of ecosystem respiration in overstory and understory flux measurements using the eddy covariance method.

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Chapter 1

General introduction

1.1 Background

Worldwide concerns about global change and its future effects on soil respiration have raised the need for exploring the biogeochemical reaction rates in soils. Soil is an important component of the global carbon budget for several reasons. After the deep ocean, soil is considered the second largest pool in the global carbon cycle, comprising more than twice the estimated pool of carbon in plant biomass (Rayment and Jarvis, 2000). Secondly, soil contributes 20–40% of atmospheric CO₂ annual input (Raich and Schlesinger, 1992), emitting about 68–100 Gt C year⁻¹ into the atmosphere (Raich and Schlesinger, 1992; Musselman and Fox, 1991) through plant root respiration and decomposition of soil organic matter (SOM) by soil microorganisms.

Although, in the last two decades a large amount of research has been dedicated to study the significance and nature of the terrestrial biosphere as a global carbon source or sink, better knowledge of carbon flow is needed to understand the importance of its role. In order to provide the inputs needed by regional and global carbon budget models, more accurate measurements of CO₂ fluxes are essential (Raich and Shlesinger, 1992; Bowden et al., 1993; Handson et al., 1993; Sundquist, 1993; Lavigne and Ryan, 1997; Buchmann

and Shulze, 1999) to quantify the soil CO₂ efflux and to predict the interaction of environmental factors on soil respiration.

Carbon flow through the biosphere may be defined as the transfer of plant, animal and microbial biomass carbon from one trophic level to another (Buyanovsky *et al.*, 1987). In this process, a significant amount of the carbon accumulated by plants during photosynthesis is partially lost in autotrophic respiration; the net gain is the net primary production (NPP). Carbon is eventually transferred to the soil in litter-fall, root turn-over, and death of individual plants, providing the substrate for the formation of soil organic matter (SOM) (Edwards and Harris 1977; Kalbitz *et al.*, 2000; Hogberg *et al.*, 2001). Ultimately, carbon is released from the soil and returned to the atmosphere by the decomposition by soil micro-organisms (Gaudinski *et al.*, 2000; Chapin III and Ruess 2001). The rate of carbon transferred through the system and deposited in the soil profile is functionally related to the biological productivity and decomposition potential of the ecosystem. When the input of carbon from primary production and output as a result of mineralization are balanced the soil organic carbon content, as well as the ecosystem, remains in equilibrium state (Buyanovsky *et al.*, 1987).

1.2 Soil CO₂ sources

Respiration is a biochemical process and occurs in cells for all living soil organisms-plant, animals and microorganisms, consuming substrates from various sources. At each of the hierarchical orders from cell to globe, soil respiration involves different sets of chemicals, physical and biological processes. Soil respiration in particular, is the combination of the activity of roots and associated rhizosphere organisms, heterotrophic

bacteria and fungi present in the organic and mineral soil horizons, and soil fauna activity (Hanson et al., 2000). Root respiration uses intercellular and intracellular sugars, proteins, lipids, and other substrates. Soil microorganisms consume all kind of substrates, from simple sugars contained in fresh residues and root exudates to complex humic acids in SOM.

To understand how the CO₂ production take places in the soil profile it is important to explore the factors affecting CO₂ production are distributed throughout the soil profile. Generally, the soil profile is stratified into a number of horizons characterized by homogeneous soil properties (such as texture, structure, consistence, porosity, and minerals), root biomass, soil carbon, temperature, moisture, CO₂ concentration, and O₂ concentration. The formation of these horizons is determined by five forming factors: climate, organisms, relief, parent material, and time. The climate that influence the chemical reactions (cation exchange capacity) that take place in the pore spaces in the presence of air and water, the organic activity, and eluviation of the soil. The organisms such as the plants that change the characteristic of the soil through the addition of organic matter, the bacteria and fungi which decompose this organic matter into semi-soluble chemical substance known as humus, and larger soil organisms (animals) that vertically redistribute this humus within the mineral matter. Land relief or terrain is used as a general term in physical geography, referring to the lie of the land. This is usually expressed in terms of the elevation, slope, and orientation of terrain features. Terrain affects surface water flow and distribution. Parent material, in soil science, means the underlying geological material (generally bedrock or a superficial or drift deposit) in which soil horizons form.

The heterogeneity of substrate quality and sources of supply make soil respiration extremely difficult to derive through simple relationships between substrate supply and respiratory CO₂ production. However, recent experiments have demonstrated that substrate supply from canopy photosynthesis has a strong control on soil respiration. A tree-girdling experiment in a Scots pine forest in northern Sweden showed that after two months without carbohydrates from aboveground photosynthesis, soil respiration declined by about 50% (Högberg et al., 2001). Root and soil respiration, for example, respond to the activity of above ground herbivores (Ruess et al., 1998), availability of nutrients (Nadelhoffer, 2000), light (Craine et al., 1999) and other factors that govern plant carbon gain. In addition to the control of soil respiration by the aboveground photosynthesis, a principal mechanism by which vegetation may control soil respiration rates is via the production of plant detritus (Raich and Tufekcioglu, 2000). In this respect, litter regulates microbial respiration in the soil. Generally, soil respiration increases with the amount of litter (Maier and Kress, 2000). Raich and Nadelhoffer (1989) found that soil respiration and litter production were positively correlated in mature forest ecosystems. Carbon substrate from SOM strongly regulates soil respiration as demonstrated in many laboratory incubations. Franzluebbers et al. (2001) collected soil samples from four regions in North America, and found that basal respiration was linearly correlated to the content of SOC. They showed that the SOC in soil from warm or dry regions was released by the microbial respiration much faster than the SOC present in soil from cold or wet regions. These differences were due to a different species composition of microbial community in the soil between the two regions. In cold and wet

regions the low microbial activity facilitated the accumulation of SOC in the soil which underwent a chemical transformation to recalcitrant SOC.

On a regional scale soil respiration is correlated with ecosystem productivity. In a comparison of 18 European forests, Janssens et al. (2001) found that the annual GPP is the primary factor influencing soil respiration. Reichstein et al. (2003) suggested that measures of vegetation productivity are necessary for modeling large-scale patterns of soil respiration. Generally, root respiration is strongly related to shoot photosynthetic activity (Heilmeyer et al. 1997), whereas heterotrophic respiration is related to the decomposition of young organic matter. Therefore both autotrophic respiration and heterotrophic respiration depend on primary productivity.

1.3 Mechanism of transport of CO₂ within the soil

CO₂ concentration in the soil air space between soil particles is an order of magnitude higher than in the atmosphere (Fernandez and Kosian, 1987; Šimunek and Suarez, 1993) resulting in a large concentration gradient from deep layers to the atmosphere. The movement of the CO₂ in the soil occurs through a continuous network of air-filled pore spaces that connect the deeper layers to the surface of the soil.

The primary mechanisms that governs the gaseous movement from the soil to the atmosphere are mass flow and molecular diffusion (Freijer and Leffelaar 1996). Mass flow takes place when gradients of gas pressure between zones moves a mass of air from high to low pressure zones. Molecular diffusion is driven by a gradient of CO₂ molecules concentration in the air and causes a migration of CO₂ molecules from zone of higher concentration to zone of lower concentration.

Diffusive transport of gases in the soil is the primary mechanism for transporting CO₂ from the soil to the atmosphere. It occurs in both the gaseous phase and liquid phase of the soil, although the diffusion through air-filled pores is the major process of CO₂ transport. In contrast, mass flow affects the CO₂ movements especially in deep soil and is affected by changes in temperature and atmospheric pressure, rainwater entering the soil pore spaces and plant water uptake (Rolston, 1986, Payne and Gregory 1988). CO₂ can also move between the soil layers dissolved in water (Simunek and Suarez 1993). However, mechanisms of gas movement other than soil diffusive transport have been shown to account for less than 10% of the CO₂ transport in the shallowest soil layers and even less for the deeper unsaturated zones (Wood and Petraitis, 1984).

At the soil surface CO₂ movement is strongly influenced by barometric pressure and air turbulence fluctuations. According to Kimball (1983), barometric pressure fluctuations and wind can cause large variation in the movement of gases in soil according to soil texture. Kimball and Lemon (1971) showed that pressure fluctuations caused by wind or air turbulences can increase gas exchange several times compared with diffusion through straw mulches and coarse gravel. Therefore, at the shallowest soil depths air turbulences may increase the relative values of diffusion coefficient above the lower limit of molecular diffusion amplifying the uncertainties of CO₂ flux measurements at the soil surface.

1.4 Factors affecting soil respiration

In general, soil temperature and soil moisture are considered the main abiotic factors influencing soil respiration and are referred to as the *primary factors*. On the other hand,

root respiration and substrate supply due to productivity and microbial interactions are the main biotic factors and are considered to be *secondary factors* that influence soil respiration. Soil respiration also varies with vegetation. Respiration rates vary significantly among major biomes types, with vegetation type and net primary productivity (NPP) being an important determinant of soil respiration rates. (Lundegardh, 1927; Reiners, 1968; Rixon, 1968, Edwards, 1974; Weber, 1990; Johnson, 1993; Mielenick and Dugas, 1999, Maier and Kress, 2000; Schlesinger and Andrew, 2000; Raich and Tufekcioglu, 2000; Kirshbaum, 2000).

1.4.1 Soil temperature

It is widely recognized the temperature is a key factor controlling soil CO₂ flux. On shorter time scales diurnal changes in soil CO₂ flux have generally been observed to follow soil temperature (Akinremi et al., 1998) with maximum CO₂ flux occurring in the mid-afternoon and minimum fluxes occurring in the early morning. But also at seasonal scales, changes of CO₂ flux have been reported to follow seasonal temperature trends (Anderson, 1973; Buyanovsky et al., 1987; Franzluebbers et al., 2002; Raich and Tufekcioglu, 2000; Rochette et al., 1991).

The quantification of the temperature dependence of soil respiration has been attempted by many studies either by the study of specific ecosystems or through reviews that summarise the results obtained in different individual studies (Kirschbaum, 2006). Commonly two types of approaches are used to relate temperature and soil respiration. The first is an empirical exponential relationship suggested by van t'Hoff (1884):

$$SR = a \cdot e^{bT} \quad (1)$$

and modified by van't Hoff in 1898 (e.g., Yuste et al., 2004):

$$SR = SRT_{ref} \cdot e^{\frac{\ln Q_{10}}{10}(T - T_{ref})} \quad (2)$$

where SR is soil respiration ($\mu\text{mol m}^{-2} \text{s}^{-1}$), T is temperature (K) and T_{ref} is an arbitrary reference temperature with a known respiration rate SRT_{ref} . Q_{10} is the rate by which respiration changes with a temperature change of 10 K. The Q_{10} is a commonly used parameter to report the temperature sensitivity of soil respiration, which is constant in Eq.(1).

The second relationship is based on and uses activation energy considerations introduced by Arrhenius (1898):

$$SR = A \cdot e^{-Ea/RT} \quad (3)$$

where A is the frequency factor ($\text{mol m}^{-3} \text{s}^{-1}$), Ea is the activation energy (J mol^{-1}), and $R = 8.314 \text{ (J mol}^{-1} \text{K}^{-1})$ is the universal gas constant. Eq. 3 can be rewritten for the reaction rate and relative to the rate at some standard temperature, in this case 283.15 K (Lloyd and Taylor, 1994):

$$SR = SRT_{ref} \cdot e^{\frac{Ea}{RT_{ref}}(T - T_{ref})} \quad (4)$$

Here, Ea is the activation energy (J mol^{-1}), and $R = 8.314 \text{ (J mol}^{-1} \text{K}^{-1})$ is the universal gas constant. The temperature sensitivity coefficients Ea is not equivalent to the above Q_{10} . A Q_{10} value derived from Eq. (4) based on Ea would decrease slowly with increasing temperature (Kirschbaum, 2006; Shi et al., 2006).

Lloyd and Taylor (1994), using a comprehensive data set of observed seasonal soil respiration, showed how the Q_{10} model of Van't Hoff and the Arrhenius equation were

biased when fitting to the data, underestimating at lower temperature and overestimating at higher temperatures. Moreover, they developed an equation that described the temperature dependence:

$$SR = SRT_{ref} \cdot e^{E_o \left(\frac{1}{T_{ref} - T_0} - \frac{1}{T - T_0} \right)} \quad (5)$$

where SRT_{ref} is a the respiration rate at 10 °C, E_o is a parameter related to the activation energy (308.56 K), T_{ref} is the reference temperature at 10 °C and T_0 is equal to 227.13 K. The modified Arrhenius model developed by Lloyd and Taylor appears to be more appropriate at higher temperature when soil respiration is suppressed (Richardson et al., 2006). However, a simulation made by Richardson and Hollinger (2005) suggested that the Lloyd and Taylor model is over parameterized because different combinations of parameters can produce versions of the model that fit the data equally well.

Currently the Q_{10} factor is widely used to describe the soil respiration-temperature relationship and for understanding ecosystem carbon dynamics in response to global change. A number of different mathematical relationships (linear, exponential, quadratic, polynomial, and logistical) (Fang and Mancrieff, 2001) have been developed to describe such biologically and physically affected relationships. However, commonly a first-order exponential model (Eq. 1), which predicts that respiration increases in a steady relative rate as the temperature increases, has been used in many branches of biology. This characteristic is a widespread criticism of the Q_{10} , and raises the question as to whether Q_{10} can be used in soil respiration data analysis and models (Richardson et al., 2006). Many studies have clearly indicated that temperature dependencies of soil respiration do not conform to the assumption of a constant Q_{10} over a wider range of temperature.

Moreover, due to the nonlinear nature of the relationship between Q_{10} and soil respiration, small change in Q_{10} may cause significant differences in estimated soil respiration. Values of Q_{10} may vary with temperature in space and time across ecosystems. Raich and Schlesinger (1992), compiling an extensive literature data set of soil respiration, showed that the value of Q_{10} varied between 1.3 and 3.3. Kirschbaum (1995) trying to separate the moisture and litter quality effects from the temperature effect, obtained an even greater range of Q_{10} from 2.5 at 20 °C to 8 at 0 °C. All these contradictory results could depend on the geographic locations and ecosystem types (Peterjohn et al., 1993, 1994; Lloyd and Taylor, 1994; Kirshbaum 1995; Cheng et al., 2000). They could be also related to the discrepancies between the methodologies used for measuring soil respiration (Pumpanen et al., 2004 and papers cited therein) and soil temperature. For example, the use of air temperature, which typically fluctuates more than soil temperature (Raich and Potter, 1995; Parkin and Kaspar, 2003), or the use of soil temperature measured at 5 or 10 cm depth with the assumption that CO₂ flux is a reflection of activity at these depths. More importantly, the reason why the temperature dependence of soil respiration is still not fully explained is because different components of soil respiration (autotrophic and heterotrophic) and soil carbon pools (pools of labile and recalcitrant substrate) may have different temperature sensitivities (Kirshbaum, 2006; Gut et al., 2004). It is still not clear whether autotrophic root respiration or heterotrophic decomposer respiration has stronger temperature dependence (Kirschbaum, 2006). In this respect, different studies have pointed out the need to better quantify the role of confounding factors which limit the understanding of the temperature dependence of soil respiration (Boone et al., 1998; Lenton and Huntingford, 2003).

1.4.2 Confounding factors affecting the soil respiration-temperature relationship

In a natural systems soil respiration is the result of a combination of autotrophic and heterotrophic respiration. Vegetation can impact on soil respiration in many ways. The temperature sensitivity of root respiration is generally affected by plant phenological factors such as the seasonality of root growth and death (Curiel Yuste et al. 2004). Atkin et al. (2000) reported that root respiration generally has a short term temperature dependency (few hours). Raich and Tufekcioglu (2000) showed how soil microclimate was affected indirectly by vegetation types. Measuring soil respiration in two agricultural fields of identical soil type, but one planted to soybeans and the other to switchgrass, they noticed how the dense cover of living and dead plant matter in the switchgrass could alter the soil microclimate and therefore the respiration rate (Figure 1) and its relationship with soil temperature.

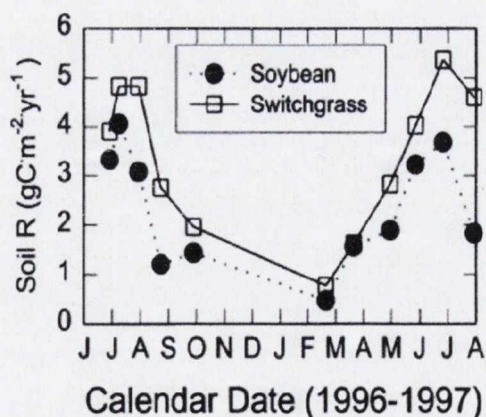


Figure 1: In situ soil respiration in central Iowa agricultural fields planted to soybean (solid symbols) and switchgrass (open squares) (Raich and Tufekcioglu, 2000).

Dead plant matter in particular is an important confounding factor in temperature dependency of soil respiration studies (Gut et al., 2004; Kirshbaum, 2006). In natural conditions changes in pools of labile substrate affects the temperature dependence of soil respiration. In essence, organic matter is characterised by the amount of labile or recalcitrant substrate which determine the quality of available substrate for the soil decomposer activity. Generally minor changes in carbon substrate availability over the seasons lead to a soil CO₂ efflux well correlated with seasonal soil temperature changes. However, in the presence of more labile soil organic matter (starch, sugar, amino acids), with a short turn-over time, the decomposition of SOM leads to a big loss of the system's carbon over a short period of time, resulting in high carbon flux in spring, when labile substrate availability in the litter is higher, rather than in summer season, despite the higher soil temperature in the summer. Hence, the fast depletion of the pool over time leads to a contraction of the temperature effects on soil respiration, and therefore a modification of the temperature dependence of soil respiration.

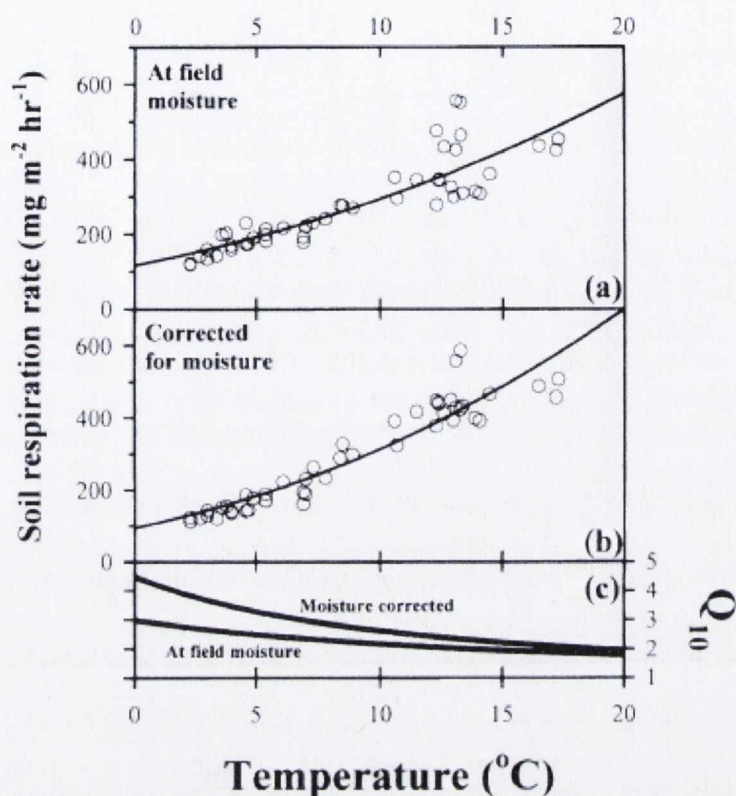


Figure 2: Respiration as a function of temperature (after Keith et al. 1997). Figure 2(a) shows data at temperatures and moisture levels observed in the field and with the Lloyd and Taylor (1994) equation fitted to the data. Each observation was then corrected for moisture by calculating a notional rate at constant moisture. The modified data are shown in Figure 6(b), and the exponential function was again fitted to the modified data. Both fitted relationships are shown on a Q_{10} plot in Figure 6(c).

Although soil moisture together with soil temperature is a primary factor affecting soil respiration, in soil respiration-temperature relationship studies soil moisture is seen as a confounding factor. Generally, the interaction of soil respiration with moisture in the description of the temperature dependence is very important. Keith et al. (1997) working in an *Eucalyptus pauciflora* near Canberra, Australia, pointed out that by correcting the respiration rate data for the effect of soil moisture, they showed stronger temperature dependence by up to 1 ½ units of the Q_{10} scale (Figure 2).

1.4.3 Soil moisture

Besides temperature, soil moisture is another important primary factor affecting the rate of soil respiration (Singh and Gupta, 1977; Davidson et al., 1998; Gullledge and Schimel, 2000; Xu and Qi, 2001). The common understanding of the relationship between soil moisture and soil respiration states that soil CO₂ efflux is low under dry conditions, reaches the maximal rate in the near field capacity, and decreases at high moisture content when anaerobic conditions depress aerobic microbial activity.

Soil water content in the field is very dynamic and fluctuates over time with stochastic events of rainfall. The stochastic events of rainfall result in a strong variation in soil respiration in natural ecosystems. Generally the phases of soil moisture effects on soil respiration over time can be summarised as: (i) A degassing effect which occurs at the initial stages of the rainfall event. During the rainfall, water infiltration fills the pores replacing the soil gases. Soil degassing is usually very quick and it is considered to be a release of stored CO₂ in soil from past soil activities; (ii) an activation of microbial activity. This stage occurs several hours or few days after the rainfall, resulting in an increase of soil CO₂ efflux. Fierer and Schimel (2003), in an attempt to identify carbon sources of the pulse CO₂ release after rewetting soil, suggested that CO₂ is generally produced by the mineralization of microbial biomass; (iii) an increase of root respiration which occurs several days after the first addition of water to dry soil. The creation of new roots growth after rewetting coupled with an improved foliage activity enhance the carbohydrates supply to roots and rhizosphere resulting in a larger ecosystem respiration.

Numerous studies have sought to establish the relationship between soil moisture and soil respiration. While there has been much consensus on modelling the effect of soil temperature on soil respiration (Lloyd and Taylor, 1994), little consensus has been achieved on the function form of the moisture effect. The inconsistent response of soil respiration to moisture content is due to complex mechanisms that involve the CO₂ production and transports processes and from fluctuation in moisture conditions in the field. However, several mathematical approaches were used in fitting the moisture-soil respiration relationship, these include: (i) linear function with volumetric water content as independent variable (Ochard and Cook, 1983; Rout and Gupta, 1989; Epron et al., 1999; Leiros et al., 1999), (ii) exponential and logarithmic functions both with water potential as independent variable (Davidson et al., 1998; Ochard and Cook, 1983), and (iii) quadratic function (Bunnell et al., 1977; Linn et al., 1984; Mielnik and Dugas, 2000; Qi and Xu, 2001).

Generally the concomitant variation of environmental factors such as soil moisture, soil temperature, leaf area index (LAI) has been assumed by ecosystem modellers to be multiplicative to describe responses of soil respiration.. Most of the models that have been developed to describe the interactive effects usually use multiplication/division and/or addition/subtraction to combine the effects of individual factors. Thus, if the effect of moisture and temperature are independent of each other, the combined effect of moisture and temperature on soil respiration has been modelled multiplying a temperature function (usually a Q_{10} function) with a moisture content function (Raich et al., 1991; Potter et al., 1993).

1.4.4 Vegetation and soil respiration

Differences in C cycling between vegetation types suggest that land cover changes would alter the soil-atmosphere C flux (Raich and Tufekcioglu, 2000). For any system in equilibrium over time, soil respiration over a year or more must equal the rate of carbon input (Kirshbaum, 2000). In line with this consideration, Raich and Schlesinger (1992) found a good linear correlation between annual soil respiration rate and NPP, with an $r^2 = 0.87$. Generally NPP has a much weaker temperature dependence than soil respiration and heterotrophic respiration in particular (Kirshbaum, 2000). This suggests that with increasing temperature soil organic carbon decomposition will be stimulated much more than NPP, constituting a positive feed-back on climate change, adding to the build up of CO₂ in the atmosphere (Kirshbaum, 2000). Moreover, the increased flux of CO₂ from soil as a result of disturbance or global warming will largely derive from labile pools with the fastest turn over (Schlesinger and Andrews, 2000).

Although vegetation has a primary role in controlling soil respiration rates *in situ* (Raich and Tufekcioglu, 2000), it has been pointed out that the contribution of vegetation itself strongly limits the use of soil CO₂ flux to determine whether or not the soil is a net source or a net sink of CO₂ (Dormaar, 1990; Cheng and Kuzyakov, 2005). Plant-derived CO₂ is produced from C with a very short mean residence time (MRT) in soil. Based on the type of vegetation, the C used by roots and rhizomicrobial activity last in the soil from few minutes to few days (Gregory and Atwell, 1991; Cheng et al., 1993; Kuzyakov et al., 1999, 2000), resulting in diurnal CO₂ dynamics that has no effect on long-term carbon balance in soils. Contrarily, the degradation of the SOM by soil microorganisms

(bacteria, fungi, actinomycetes and protozoans) can last from weeks to hundreds of years (Cadisch and Giller, 1997, Gaudinski et al., 2000, Hahn and Buchmann, 2004), forming the most important source of soil CO₂ efflux and therefore a crucial tool to estimate C balance of ecosystems.

1.5 Temporal and spatial variation of soil respiration

Soil respiration can vary at a temporal and spatial scale. Generally the temporal variation is characterized by diurnal, weekly, seasonal, interannual, and decadal scale. While the spatial variation from few centimeters, to global scale.

On a daily basis, soil respiration closely follows soil temperature, reaching a peak at noon, early afternoon, and then declines throughout the afternoon and the night to reach a minimum in the early morning. The diurnal variation of soil respiration can be a source of errors when estimates of annual soil effluxes are made using daily point measurements. Davidson et al. (1998) found that midmorning flux, from 9 to 11 am, better resembled the 24 hour mean flux than did measurements made at the warmest part of the day, which overestimated the daily mean rate of about 4-6%. Therefore, caution should be taken when daily measurements are used to estimate monthly or annual soil CO₂ effluxes. Diurnal soil respiration is also correlated to substrate supply coming from the photosynthetic activity of aboveground plants. Generally, the correlation between soil respiration and photosynthesis has been reported to have a time delay ranging from 7 to 12 hours (Tang et al., 2005a; Moyano et al., 2008). In addition, diurnal patterns of soil respiration can be affected by rainfall events and atmospheric pressure changes at diurnal scale.

On the weekly basis, soil respiration is generally affected by synoptic weather changes associated with phases of low and high atmospheric pressure. Synoptic weather can also cause periods of clear sky, overcast, or partially cloudy condition, which alter the available light to the ecosystem, changes of soil temperature, and humidity affecting photosynthesis and respiration.

The seasonal variation of soil respiration is more related to the type of ecosystem and climate. Generally, we can observe in almost all ecosystems higher CO₂ efflux in the summer and lower in the winter. These changes are driven above all by temperature, moisture, aboveground plant activity or production/respiration. In arid or semiarid ecosystems, soil moisture is the main factor limiting soil respiration (Davidson et al., 2000), in tropical rainforests, in temperate forests and grasslands, temperature and solar radiation are the main drivers (Hanson et al., 1993; Epron et al., 2001; Borken et al., 2002), and in Mediterranean ecosystems temperature regulates the CO₂ efflux during the winter periods and moisture constrain the biological activity in the summer (Rey et al., 2002; Inglima et al., 2009). However, on a global scale, soil respiration reaches the maximum during the summer season when plant growth is active in the temperate and equatorial regions (Raich and Potter 1995, Raich et al., 2002). In this respect, plant phenology has an important influence on soil respiration, mainly through different timing of root growth, root turnover, and litter fall. The amplitude of the seasonal changes in CO₂ efflux is positively correlated with changes of LAI, a measure of deciduousness of the vegetation.

Finally the interannual and decadal variability of soil respiration strongly depend on the variability of the climate from year to year (Epron et al., 2004), changes in

physiological process like growth season length, phenology (Weber et al., 1990), and change in nutrient availability (King et al., 2004).

1.6 Responses of soil respiration to disturbances

Disturbances affect soil respiration through the modification of the individual environmental factors and biological factors. Generally, the disturbances include the rising CO₂ concentration, climatic warming, fertilization and agricultural cultivation.

Elevated CO₂ concentrations in the atmosphere generally increase soil CO₂ emissions. Rising atmospheric CO₂ stimulates plant photosynthesis and growth, changing the substrate supply to the rhizosphere. An increase in CO₂ concentration between 200 and 350 ppm usually stimulates photosynthesis by 40 to 60% (Ceulemans and Mousseau, 1994; Medlyn and Jarvis, 1999). The increase in photosynthesis and plant biomass growth result in an increase of litter production, an increase of microbial activity, an increase of carbon substrate delivered belowground which stimulate the root respiration, root biomass, and root turnover rates. Moreover, Luo et al. (2006) averaging 186 paired observations, from several Free Air Carbon Enrichment (FACE) studies carried out in USA, and Europe, found that above ground biomass growth by 22.4%. Moreover, belowground biomass was enhanced by 31.6%, with fine –root production and turnover by up to 96%.

Climate warming generally increases CO₂ efflux from soil. As discussed above, soil respiration is sensitive to soil temperature, and most modelling studies assume that soil respiration would double per 10 °C increase of soil temperature (Q_{10}). However, climate warming affects soil respiration directly and indirectly by modifying the growing season

(Lucht et al., 2002; Norby et al., 2003), altering plant phenology (Dunne et al., 2003; Fang et al., 2003), stimulating plant growth (Wan et al., 2005), increasing mineralization (Rustad et al., 2001), changes the precipitation frequency and intensity, and altering species composition and the community structure. All these effects differ with location, and the magnitude of the response of soil respiration is greater in cold, high altitude ecosystems than in warm, temperate areas (Kirschbaum, 1995; Parton et al., 1995). However, due to acclimatization the responses of soil respiration to global warming decrease over time (Luo et al., 2001a). In a soil-warming experiment carried out in New England, the CO₂ efflux was about 40% higher than that in the control plots in the first year, but after six years of warming treatment the warming effect disappeared. Luo et al. (2002) indicated that acclimatization to global warming results in a decrease of temperature sensitivity. They showed that in a warming experiment on a field of tallgrass in Oklahoma, the Q_{10} value decreased from 2.7 to 2.4. As discussed in the section 1.3, this is likely due to a faster decomposition rate of labile soil carbon pool, also called a confounding factor in temperature sensitivity studies (Kirschbaum, 2004). Finally, warming causes a shift in the soil microbial community structure in the soil towards fungi which are more tolerant than bacteria to high soil temperature (Holland and Coleman 1987). This contributes to decrease the decrease in sensitivity of soil respiration to soil temperature changes.

Generally, agricultural cultivation improves soil aeration and moisture conditions resulting in an increase in the mineralization of the SOM and therefore increasing soil respiration (McGuire et al., 2001). However, over time the depletion of soil substrate results in a reduction of soil respiration. Wang et al. (1999) showed that in southern

central California, after 22 years of conversion of an annual grassland to a lemon orchard the soil carbon content decreased by 26%, and as a result annual soil respiration decreased by 11% with litter and by 31% without litter. Therefore, land use change, particularly the conversion of forest lands to other land covers and uses, is a primary way in which humans are altering the global C cycle (Conway et al. 1994, Schlesinger 1997). Forest conversion to agriculture has historically been the most common land use change, and typically results in the reduction of terrestrial carbon pools (Davidson and Ackerman 1993, Pennock and Vankessel 1997), although the amount and rate of C loss also depend on agricultural practices (Buyanovsky et al. 1987, Buyanovsky and Wagner 1995). Nowadays, afforestation, reforestation and deforestation (article 3.3 of Kyoto protocol) and improved managements of agricultural soils (article 3.4) are considered valuable actions for reducing CO₂ emission among the parties that ratified the United Nation Framework Convention on Climate Change (UNFCCC).

1.7 Methods for measuring soil respiration

There is no doubt that without accurate techniques to measure CO₂ concentration and calculate soil CO₂ efflux we could not study the processes of soil respiration, evaluate the magnitude of soil respiration of different ecosystems and develop models to simulate soil respiration in new environmental conditions.

The transport of CO₂ in the porous medium of soil is extremely complex and any measuring method that disturbs the soil CO₂ concentration and modifies the gradient can cause errors in CO₂ flux measurements. Currently, no single method has been established

as a standard, and soil respiration can be measured at the soil surface or estimated measuring CO₂ concentrations within the soil profile.

1.7.1 Soil Respiration Chambers

The use of soil respiration chambers is the most common and simplest method to measure CO₂ flux from soil surface, and can be distinguished between manual and automated chamber systems (Savage and Davidson 2003; Liu et al., 2006; Carbone and Vargas, 2008). Manual measurements are usually made at discrete points in time (weekly or less frequently) but with sampling across the landscape, and achieved with relatively inexpensive instruments. Due to equipment constraints, manual sampling occurs only during days without precipitation, missing the immediate effect of soil moisture changes on soil respiration (Lee et al., 2004; Xu et al., 2004). Automated soil surface chambers can function without supervision for continuous and semi-continuous measurements (Drewitt et al., 2002; King and Harrison, 2002), providing a consistent body of data which permit modelling and statistic analysis of soil respiration at time scale from minutes to months. However, their high initial cost, and limited number of fixed sampling measuring points means the manual chambers remain the most frequently used option among soil scientist.

Despite the popularity of this technique, protocols for evaluating soil surface chambers data quality have not been fully addressed (Savage et al., 2008). However, several publications have compared different designs of soil surface chambers and addressed their sources of errors (Hutchinson and Livingston 2001; Davidson et al., 2002). In

essence, the surface chamber design should: (i) minimize the alteration of soil respiratory activity by changes in natural microclimate within the chamber or disturbing the soil surface during deployment, (ii) do not cause changes in air pressure within the chamber, and (iii) do not modify the natural soil profile CO₂ concentration gradient by building up of CO₂ concentration within the chamber.

1.7.2 Soil profile gradient approach

The soil CO₂ gradient approach has been proposed as an alternative to surface chambers for measuring CO₂ efflux, and more importantly to explore the vertical process of soil respiration and their contribution to the soil CO₂ production (Hirano et al., 2003; Tang et al., 2003, 2005; Turcu et al., 2005; DeSutter et al., 2008).

The main assumption of the gradient approach is that diffusion is the major process of transport which moves the gas vertically in the soil profile. The measurement of CO₂ concentrations at different soil depth result in the formation of the CO₂ gradient through the soil profile. The gradient together with the soil CO₂ diffusion coefficient is used to calculate soil respiration in each layer. This calculation is often made using Fick's Law:

$$F = D_s \frac{dC}{dz} \approx D_s \frac{\Delta C}{\Delta Z} \quad (6)$$

where F is the flux of CO₂ ($\mu\text{mol m}^{-2} \text{s}^{-1}$), D_s is the soil diffusion coefficient of CO₂ in the soil ($\text{m}^2 \text{s}^{-1}$), C is the concentration of CO₂ ($\mu\text{mol m}^{-3}$), and z is the depth below the soil surface (m).

The gradient approach is highly dependent on soil diffusivity, which varies with soil porosity and tortuosity. Studies have either used published D_s models (Davidson et al., 2006; Pumpanen et al., 2005; Tang et al., 2003, 2005; Turcu et al., 2005; DeSutter et al., 2008) or determined D_s values specific to their soils (Davidson et al., 2006; Hirano et al., 2003; Jassal et al., 2004, 2005; Liang et al., 2004; DeSutter et al., 2008). In general, the difficulty in estimating the soil diffusivity depends on the influence of soil moisture and soil temperature on modifying D_s . The majority of the models make the simple assumption that D_s is reduced in proportion to the reduction in air-filled pore spaces caused by soil moisture content changes. However, Šimůnek and Suarez (1993) noted that the use of soil moisture for calculating D_s leads to an underestimation of the CO_2 flux. Additional difficulty of the gradient approach is determined by the estimation of the soil vertical CO_2 gradient using more than two CO_2 measuring points in soil profile. Numerous researchers have failed to report the model used to describe the concentration gradient related to the multiple measuring points (DeSutter et al., 2008). DeSutter et al. (2008) showed that the use of three different existing models, the linear regression model (Tang et al., 2003), power function model (Davidson et al., 2006), and the finite-difference approach (DeSutter et al., 2008), resulting in substantial disagreements using the same data-set.

Generally, CO_2 flux estimations using the gradient approach can be achieved by: (i) the manual gas extraction approach, and (ii) the in-situ gas concentration approach. Although sometimes these two categories could be applied to the same type of soil profile techniques (discussed in more detail in Chapter 3), their fundamental difference is that the in-situ approach allows the continuous or semi continuous measurement of soil air

directly in the field using above ground IRGAs connected to the below ground soil probes by automated multiport sampling channels (Hirsch et al., 2002; DeSutter et al., 2008; Albanito et al, 2009), whereas, the gas extraction approach requires the manual withdraw of soil air using syringes, and subsequent laboratory analysis of the air samples by injecting them into an IRGA or a Gas Chromatograph (De Jong and Schapper 1972, Wagner and Buyanovsky, 1983; Goodroad and Keeney 1985, Burton and Beauchamp, 1994; Davidson and Trumbore, 1995; Fang and Moncrieff 1998; Kammann et al 2000). The common key advantage of both these approaches are that they do not alter the soil surface boundary conditions like surface chambers (DeSutter et al., 2008), they can easily be adapted to sample other soil trace gases such as nitrous oxide (N_2O) and methane (CH_4), and finally they could be used to perform *in situ* extraction of ^{12}C and ^{13}C isotopes of CO_2 . However, the manual gas extraction approach does not provide continuous measurements of soil CO_2 concentration. Furthermore, it has an unavoidable shortcomings due to gas extraction processes, storage, transport and measurement.

In the recent years a new variant of the in-situ approach has been attempted by burring at different soil depths solid-state CO_2 sensors, developed primarily for air quality monitoring and control (Hirano et al., 2000; Tang et al., 2003; DeSutter et al., 2008). This method is useful as it allows the measurement of short-term changes in belowground CO_2 concentration and offers a vast improvement in the temporal resolution of CO_2 production and gradient-based soil CO_2 fluxes. However, there are significant shortcomings associated with the solid state probes. In particular changing humidity with the soil profile may influence the small non-dispersive infrared (NDIR) sensors. Although an impermeable membrane protects the NDIR sensor, in flooded and saturated

soil especially following heavy rain, the probe needs to be retrieved from the soil profile for essential maintenance; making the use of the solid-state sensors unsuitable for long term and deep soil profile studies. Furthermore, in order to avoid condensation on the NDIR sensor and the sensor electronic parts, the probe has to be powered on continuously with the disadvantage of modifying the temperature of the soil surrounding the sensor.

Due to the above difficulties, methods to estimate CO₂ efflux using the concentration gradient approach are still in development and have become the focus of scientific research during the last decade. Vertical partitioning of the sources of CO₂ production is a critical factor for understanding soil carbon dynamics (de Jong and Schappert, 1972; Hendry et al., 1993; Davidson and Trumbore, 1995; Gaudinski et al., 2000; hashimoto and Suzuki, 2002; Hirsch et al., 2002, 2004; Jassal et al., 2004, 2005; Davidson et al., 2006). Moreover, it is important to investigate soil respiration at several depths and investigate the response of deep-soil respiration to different environmental conditions (Hashimoto et al., 2006).

1.8 Methods for partitioning sources of CO₂ efflux from soil

In the last decade several reviews of partitioning methods to estimate the contribution of individual sources to total soil CO₂ efflux have been published (Hanson et al. 2000; Baggs 2006; Subke et al., 2006; and Kuzyakov 2006). Despite their differences in categorizing the numerous partitioning methods used worldwide, they all agreed that the separation and estimation of the true autotrophic and heterotrophic respiration is still a real challenge for the current ecosystem research. In essence, the natural absence of sharp boundaries between root and rhizomicrobial respiration and the current methodological

limitation on separating these two sources are the basis of the problem. Nowadays, the precise source of autotrophic respiration remains an open dispute between soil microbiologist and ecosystem ecologist. The first asserting that root respiration should not been combined with the activity of taxonomically different microorganism (mycorrhizal fungi and other rhizosphere microorganisms) within autotrophic respiration (Kuzyakov, 2006). Whereas the second, consider the lumping of the root cells with rhizosphere microorganisms justified by the fact that both of them are strongly dependent on recent plant canopy photosynthate for their respiratory activity (Högberg et al., 2006).

The partitioning of soil respiration is an important issue in forest ecosystem ecology, carbon cycling, plant physiology, soil science, and global climate change modelling (Bond-Lamberty et al., 2004). Different components could respond differently to temperature, resulting in different soil flux behaviours for a variety of time scales and for different plant species. In addition, while measurements of net primary production (NPP) subsume autotrophic respiration losses, knowledge of heterotrophic fluxes is required to calculate net ecosystem production and permit comparison of process- and biomass-based estimates with net ecosystem exchange derived from eddy covariance techniques (Bond-Lamberty et al., 2004). Thus the contribution of each component of soil respiration is crucial to understand the effects of global change on net exchange of CO₂ between terrestrial ecosystems and the atmosphere (Bond-Lamberty et al., 2004).

Here is reported a brief description of the classification adopted by Subke et al. (2006) for field and laboratory methods, which strongly referred to Hanson et al. (2000). The soil CO₂ efflux measurements were separated into: (1) root exclusion, (2) physical separation of components, (3) isotopic techniques, and (4) indirect methods. Considering the

complexity of the indirect methods or modelling approaches, I refer the reader to Subke et al., 2006 for further descriptions.

1.8.1 Root exclusion

Trenching. This technique relies on severing all roots around the perimeter of the treatment plot in order to disrupt aboveground input from trees (e.g. Epron et al., 1999).

Girdling. Technique applied to forest stands only. During stem girdling, the bark is removed over several centimetres around the circumference of all trees within the treatment plot. This treatment allow the trees to maintain water transport from the roots to the crown in the xylem, while disrupting the transport of assimilates from the crowns to the roots in the phloem, as the cambium is removed with the bark (e.g. Högberg et al., 2001).

Clipping. Applies to grassland and shrub communities, where all aboveground parts of the plants are clipped and removed, leaving the root system intact, but starved of aboveground input (e.g. Wan and Luo, 2003).

Gap. In order to estimate the amount of CO₂ from live root respiration, above ground vegetation is removed (clear-cut) from a relative large area (e.g. Nakane et al., 1996). Differences between total CO₂ efflux rate in unmodified areas and CO₂ flux rate in clear-cut areas gives indirect estimates of autotrophic respiration.

1.8.2 Physical separation of components

Components. This category includes all studies that have separated soil cores taken in the field to measure the respiration of some or all of its components (surface litter, roots, and SOM) in isolation in order to assess individual contributions (e.g. Thierron and Laudelout, 1996).

Root excising. This technique relies on measuring the CO₂ produced by roots shortly after being recovered from a fresh soil core (e.g. Law et al., 2001b). The root contribution is then calculated using this flux and estimates of root density in a stand, and measurements of undisturbed soil respiration.

Live root respiration. Following the careful excavation of entire roots these are enclosed in a cuvette while still attached to the plant, to measure CO₂ production by roots directly (Kutsch et al., 2001b).

1.8.3 Isotope techniques

Isotopic labelling. Isotopic labels (¹³C) introduced in CO₂ enrichment experiments (e.g. FACE, open top chambers or growth chambers) have been used to separate plant derived CO₂ within total soil respiration (e.g. Andrews et al., 1999). Another possibility is to replace one or more soil components with isotopically labelled components (e.g. in soil transplant studies, where C₄ plants are grown on soils previously dominated by C₃ plants, or vice versa; e.g. Rochette and Flanagan, 1997). The basis of this approach is that the different photosynthetic pathways have specific isotopic fractionations. By growing the

different plant type respectively different soils, it is possible to distinguish between the older (i.e. SOM and old litter)-derived CO₂ and fresh plant-derived CO₂. Pulse labelling, or repeated pulse labelling using either ¹³C or ¹⁴C is also used to partition C assimilated by plants between plant and soil pools and respective respiratory fluxes (e.g. Meharg, 1994).

Radiocarbon. The radioactive decay of the ¹⁴C isotope allows organic matter to be dated as its D¹⁴C value reflects the atmospheric value at the time of photosynthetic assimilation. As single measurements of the D¹⁴C value of soil respired CO₂ reflect a mixture of sources, this technique requires additional modelling to disentangle individual components that have contributed to the overall efflux.

1.9 Motivation and objectives of the thesis

It is widely accepted that more studies are required to enhance our understanding of the role of soil processes in controlling soil respiration. The contribution of the deep organic horizons to soil CO₂ efflux still remain unclear, as does the effect of climate change on deep soil processes. The impact of global warming on soil respiration is strongly related to the characteristics of deep-soil carbon and may differ with soil depth. Environmental parameters can affect the rates of soil CO₂ respiration not only temporally at daily and seasonal scale, but also spatially in vertical and horizontal dimensions. Therefore, it is important to evaluate soil subsurface CO₂ production and investigate the seasonal response of deep-soil respiration to different environmental conditions.

Measuring soil respiration through soil profile studies can be challenging because the CO₂ efflux from soil integrates several complex below-ground processes and fluxes, such

as respiration by roots, mycorrhizae, rhizosphere, and saprophytic microbes. In this respect, accurate techniques used to monitor the soil CO₂ concentrations profile offer the opportunity to identify localized sources and potential sinks of CO₂ in the soil, and to understand the processes that control CO₂ production and emission. Given these research needs, the main objectives of this dissertation are:

- To propose and evaluate a new method to continuously measure high temporal resolution CO₂ concentrations throughout the soil profile.
- To calculate the high temporal resolution CO₂ efflux using a site-specific soil profile CO₂ diffusivity and gradient-based model.
- To compare and examine differences between estimated gradient-based CO₂ efflux and measured surface CO₂ efflux.
- To explore diurnal, weekly, and seasonal patterns of CO₂ effluxes, in relation to soil temperature, soil moisture and other environmental parameters.
- To evaluate the relative contribution of CO₂ production by generic soil profile layers, to report their seasonality, and to explore the dependency of CO₂ production rates to soil temperature, water content and other environmental parameters throughout the soil profile.

1.10 Outline of the thesis

Based on the objectives stated above the present dissertation consist of the following Chapters:

Chapter 1 is an introduction chapter which gives an overview of the literature concerning soil respiration, and different factors influencing CO₂ emission from soil. The components, processes, main environmental drivers, and the common techniques used for measuring CO₂ efflux from soil of soil respiration, are described in this chapter.

Chapter 2 presents a new technique “Soil diffusion chambers” for measuring continuously CO₂ concentrations in the soil profile. This chapter gives an overview of the literature concerning past techniques developed for measuring soil CO₂ concentration profiles, and discusses in details how I developed the soil diffusion chamber technique, as well as its technical characteristics. In addition, CO₂ concentrations in soil profile from 0 to 80 cm depth monitored in two sites under *Miscanthus x giganteus* during the year 2007 are reported and examined.

The use of soil profile CO₂ concentrations to estimate CO₂ efflux at soil surface is explored in Chapter 3. Here, high temporal resolution of diurnal, weakly, and seasonal variation of estimated CO₂ effluxes during the year 2008 is examined and compared to continuous CO₂ efflux measured at soil surface.

In Chapter 4 the contribution of four soil profile layers to soil CO₂ production is evaluated, as well as the seasonality of soil production rates, and the relationship to soil temperature, water content and other environmental parameters throughout the soil profile.

Finally, Chapter 5 presents conclusions and perspectives arising from this thesis

Chapter 2

¹Automated diffusion chambers to monitor diurnal and seasonal dynamics of the soil CO₂ concentration profile

Summary

To better understand the factors controlling carbon dioxide (CO₂) production and transport in soil, we developed a new method to continuously monitor soil CO₂ concentration at multiple depths, by using diffusion chambers. The soil diffusion chambers are constructed from a high-density polyethylene cylindrical frame enclosed by a micro-polyvinylidene difluoride flat membrane (PVDF). All chambers are linked to an infrared gas analyser positioned above-ground through a multi-port valve system. We set up two experimental sites for long term measurements of soil CO₂ concentration, soil temperature and soil water content at depths of 0, 10, 20, 40 and 80 cm. The system provides the following advantages : (i) the use of the PVDF combined with the small dimensions of the diffusion chambers allows rapid diffusion of soil gas into the chambers and therefore a short equilibration time of the gas phase with the surrounding soil atmosphere, (ii) the equilibrating close loop system allows the semi-

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continuous measurement of soil profile CO₂ concentrations without creating a pressure differential within the chambers, thus reducing gas concentration distortions in the soil, (iii) the small size of the closed diffusion chambers reduces the initial soil disturbance during installation, (iv) it allows sampling in wet, humid soils, including ones that are waterlogged or temporally saturated and (v) the chambers do not require removal for maintenance purposes and are inexpensive.

2.1 Introduction

In recent years soil carbon dioxide (CO₂) emissions have been the subject of intense investigation because (i) of its potential role in amplifying global warming (Trumbore *et al.*, 1996; Cox *et al.*, 2000; Giardina and Ryan, 2000; Luo *et al.*, 2001) and (ii) gaseous compounds formed in the soil are, in general, good indicators of soil biology and biochemistry (Jacinthe and Dick, 1996). Accurate techniques used to monitor soil CO₂ concentrations profile offer the opportunity to identify localized sources and potential sinks in the soil, and to understand the processes that control CO₂ production and emission.

To date, several methods have been developed to measure CO₂ concentration within the soil profile. Almost all published techniques have included some kind of spatial opening between the soil matrix and the surrounding air to allow the exchange of gas between the sampling device and the soil. Early methodologies utilized capillary tubes (Hack, 1956; Tackett, 1968; Roulier *et al.*, 1974) to investigate soil gas concentrations under field conditions by extracting gas samples directly from the soil pores. Burton and Beauchamp (1994) and Sotomayor and Rice (1999) reported a soil gas sampling technique using vertically

inserted tubes and with sample inlets placed at the desired sampling depth within the soil profile. Goodroad and Keeney (1985) and Cates and Keeney (1987) used polyvinyl chloride pipes, with 20-ml volume, installed vertically and connected to a capillary tube to sample soil air. Taylor and Abrahams (1953), Tackett (1968) and Patrick (1977) used diffusion chambers of 10-50 ml volume installed in the soil that allowed gas concentrations to reach equilibrium following diffusion of the soil atmosphere through holes of suitable size. All these diffusion techniques have no physical boundary to separate the gas phase and the surrounding soil/water and therefore have the disadvantage that they may not be suitable in flooded soil conditions. Moreover the gases withdrawal may reduce the pressure around the probe causing gas suction from undefined depths.

Fang and Moncrieff (1998) used rectangular gas traps with holes (2.5 cm × 2.5 cm × 5 cm) buried at different depths and connected to a pump that allowed the circulation of soil air between the gas trap and a sampling device at the soil surface. Their novel approach had the advantage that gas concentration equilibrium was achieved between the soil gas-trap and the above-ground sampling device reducing the uncertainty associated with sampling soil gases. However this system had the disadvantage that it was open to the soil matrix, allowing water to enter the gas trap under flooded conditions and for gas from undefined depth to be circulated within the closed loop gas circuit. Furthermore, problems associated with the back-filling of soil surrounding the trap could cause the blockage of the gas trap holes.

The idea to use silicon gas permeable tubing for sampling air was first tested and reported by Holter (1990). The concept behind this idea was to have a physical gas permeable barrier, to separate the soil/water phases from the gas phase. Several methodologies have used closed

diffusion chambers constructed with gas permeable tubing (Holter, 1990; Jacinthe and Dick, 1996; Nielsen *et al.*, 1997; Kammann *et al.*, 2001) or gas permeable membranes (Kasparov *et al.*, 1985; Panikov *et al.*, 1993) have been reported in the literature. The diffusion properties of gas-permeable membranes or tubing may be a function of the gases of interest and the timescale of the experiment may be an important factor in determining the sampling frequency. Commonly, closed diffusion chambers are constructed with polymers such as polypropylene (Gut *et al.*, 1998; Schmid *et al.*, 2001), silicone (Holter, 1990; Kramer and Conrad, 1993; Jacinthe and Dick, 1996), porous Teflon (Parkin and Tiedje, 1984; Hirsch *et al.*, 2004) and polyethylene (Namiesnik *et al.*, 2005). Closed diffusion chambers remove or reduce problems associated with pressure differentials between the diffusion chamber and the surrounding soil; hence they have the advantage of not generating mass flow in the soil matrix from undefined depths. Furthermore, they are suitable in wet or flooded soil conditions. However, depending on the type of physical barrier, soil characteristic and sampling technique, these methods may have temporal sampling resolution of hours or days. Furthermore, depending on the dimension of the gas permeable tubing and the soil sampling depth, the disadvantage of the initial disturbance of the soil at installation must be taken into consideration.

Accuracy of soil gas profile analysis depends largely on the equilibrium established between inner volume of the sampling device and the surrounding soil. In an attempt to improve sampling techniques, Panikov *et al.* (2007) reported a study on monitored soil gases within a soil profile which used a membrane probe array combined with a sampling system able to improve the sampling temporal resolution. In essence, by flushing the membrane probe

with carrier gas and converting the system from dynamic to a steady state system, they improved the temporal resolution to one sample per minute. Despite the promising results of this study, and depending on the temporal resolution of flushing the membrane probe, this technique results in the siphoning of soil gases around the probe, thus distorting the gas profile in the soil. Gut *et al.* (1998) developed a membrane tube technique (METT) to monitor soil trace gas concentrations, which used a closed-loop system similar to that adopted by Fang and Moncrieff (1998). Their study showed the importance of recycling the gas phase during the measurements in order to minimize the concentration difference between the soil and the air flowing in the membrane tube, thereby reducing gas concentration distortions in the soil. More recently, DeSutter *et al.* (2006) showed that the diffusion performances of the gas permeable tubing and the closed diffusion chambers may be improved by using an equilibrating closed loop system.

The exposure of the permeable membranes to the soil environment may influence the integrity of their diffusion properties. The integrity of the membranes, as a result of exposure to micro- and macro-fauna, should also be considered (DeSutter *et al.*, 2006). Furthermore, Rothfuss and Conrad (1994) determined, with scanning electron microscopy, that bio-films were present on silicone membranes following a one-day exposure in paddy soil. They concluded that the presence of biofilms might produce biogenic gases able to influence the concentrations of the biogases in the soil probes.

In this paper we describe a new soil diffusion chamber system, designed to combine the advantages of some of the methods described above and to overcome some of their disadvantages, while allowing the continuous measurement of CO₂ within the soil profile. This

methodology utilizes static chambers, enclosed by a polyvinylidene difluoride membrane (PVDF), positioned at the soil surface and buried in the soil profile to a depth of 80 cm.

2.2 Material and methods

2.2.1 *The experimental site*

Measurements were carried out at the Teagasc Irish Agricultural Research Institute Oak Park, Crops Research Centre, Carlow, Ireland (52° 51' N, 6° 54' W, 50 m above sea level). The study was conducted on an 13 year old *Miscanthus x giganteus* stand with a stem density of 42.5 m⁻². The soil was classified, following the classification scheme for England and Wales (Avery, 1980), as a brown podzolic soil of approximately 90-100 cm depth. The soil profile at the site was examined from the soil surface down to the bedrock and two well developed soil horizons were identified. There was a sandy silt loam A horizon from the soil surface to a depth of 35 cm, and a sand with gravel Bh horizon from a depth of 30 cm down to the bedrock at approximately 100 cm.

2.2.2 *Soil diffusion chambers*

The soil profile diffusion chamber consists of three parts: i) a high density polyethylene (HDPE) cylindrical frame, ii) a micro polyvinylidene difluoride (PVDF) flat membrane (American Membrane Co., Ltd, Nantong RC) and iii) a cylindrical metal mesh frame (1×1 cm)

and a plastic mesh net (1×1 mm) to protect the PVDF membrane from soil mesofauna (Figure 1). The cylindrical HDPE chamber has an inner volume of 365 cm³ (height 11 cm, diameter 6.5 cm), and approximately 45% of the surface area of the chamber was made gas permeable by cutting out an area of approximately 102 cm². The PVDF membrane covering the inside of the HDPE chamber is CO₂ permeable (Briscoe *et al.*, 1998) and hydrophobic, has a wall thickness of 0.06-0.08 mm and a nominal pore size of 0.2 µm. As shown in Figure 1, the physical protection of the chamber provides a small buffer volume which reduces the influence of any potential pressure or temperature fluctuations between the chamber volume and surrounding soil pore spaces.

2.2.3 Surface diffusion chamber

Near the soil surface, CO₂ transport is strongly influenced by fluctuating air pressure caused by atmospheric turbulence. Studies have shown that wind turbulence causes pressure fluctuations with a temporal duration of up to one minute near the soil surface (Agarwal *et al.* 1995, Massmann *et al.* 1997, Tackle *et al.* 2003). Such atmospheric perturbations cause vertical fluctuations in gas movement in the upper soil and can hamper soil CO₂ measurements.

In an attempt to develop a system which reduces potential pressure gradients at the soil-air-atmosphere interface, a diffusion chamber has been developed which operates at the soil surface and intercepts soil gas diffusing from the soil surface to the atmosphere (Figure 1). The chamber is constructed from the same HDPE cylindrical frame and has the same volume

as the profile diffusion chamber; and differs only by having the upper and lower surfaces open. The lower surface of the chamber is permanently positioned on the soil surface and allows the soil gas to diffuse into the chamber, while the upper surface of the chamber is covered by the PVDF membrane. Soil CO₂ diffuses from the soil surface, is thoroughly mixed in the chamber, and then diffuses through the PVDF membrane at the top of the chamber into the atmosphere.

The surface chamber has nylon tubing attached on opposite sides of the chamber. The lower tube draws the gas sample, whereas the upper tube (at approximately eight cm from the soil surface) returns the sampled gas to the chamber achieving a closed loop system (Figure 1).

2.2.4 Field installation and operation

In September 2006, two locations for the gas profile system were selected and were set up approximately 10 m apart. At both locations, one surface diffusion chamber and four soil diffusion chambers were placed on the surface (0 cm) and at depths of 10, 20, 40 and 80 cm in the soil by digging vertical holes 10 cm in diameter. The holes were then backfilled with soil in the same horizon sequence as was originally extracted.

Both the surface and the soil diffusion chambers were connected by a pair of nylon sampling tubes of approximately one meter length which had an inner and outer diameter of 0.4 and 0.6 cm, respectively, to a multi-port valve system (ACL s.r.l, 20040 Cavenago di Brianza, Milan, ITALY), which feeds the gas sample into an infrared gas analyzer (Environmental gas monitor WMA-2; PP Systems Hitchin, Hertfordshire UK) with a flow

rate of 50 ml min^{-1} . One tube drew the gaseous sample from the chamber while the other returned it to the chamber after analysis, thereby creating a closed sample loop of 100 cm^3 of volume.

At both sample sites, the multi-port solenoid system performed a daily routine of nine sub-cycles measurements. Each sub-cycle measurement of 150 minutes allowed the sequential measurement of all five chamber depths for a duration of 30 minutes. Therefore, the duration of one daily cycle was $(30 \times 5 \times 9) = 1350 \text{ min}$, *i.e.* 22.5 hours. Between each sub-cycle measurement, the gas analysers were calibrated with a two-way solenoid valve which linked for one minute the two sides of the multi-port valve system (Figure 1).

Soil volumetric water content and soil temperature were measured continuously alongside the chambers at depths of 0, 10, 20, 40, 80 cm, with dielectric sensors (ECH2O EC-5 Decagon Devices, Inc., 950 NE Nelson Court, Pullman, WA, USA) and custom-manufactured Cu-Constantan thermocouples. Hourly measurements of precipitation were obtained with a tipping bucket rain gauge (Model ARG100, Campbell Scientific Ltd, Leicestershire, UK) and horizontal wind speed and direction was measured with a vane anemometer (Model 05103, R.M. Young Co., Traverse City, MI, USA).

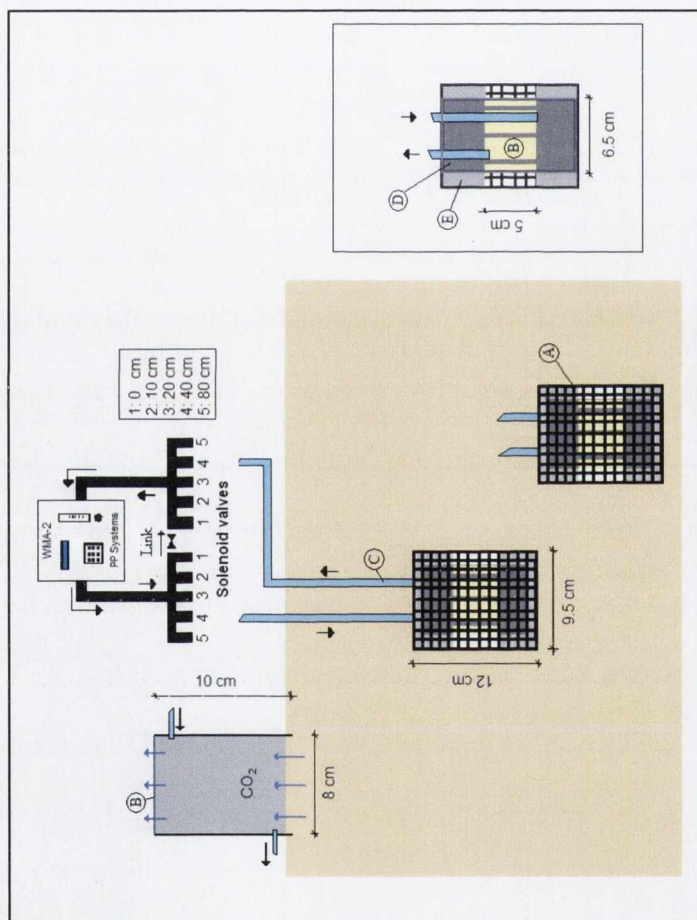


Figure 1: Schematic of the multi-port solenoid valve system for measuring soil CO₂ concentration including outer specifications of the surface diffusion chamber and soil diffusion chambers inserted in soil air-filled porosity. A, Metal net; B, PVDF membrane; C, nylon tube; D, HPDE chamber frame; E, sealing polyurethane foam. Arrows along the tubes indicate the direction of gas flow. Section on right side shows inner specifications of the soil diffusion chamber.

The output signals of the two gas analysers were collected every second and, because of the processing and memory constraints of the datalogger, were integrated over five minutes. The averaged values were then stored on a datalogger (21-X, Campbell Scientific Inc.) Finally a tube solarimeters (Delta-T devices, Cambridge, England) was installed outside the *Miscanthus x giganteus* stand for measuring solar radiation. Output signals from soil moisture probes, thermocouples, rain gauge, anemometer, and tube solarimeters were recorded every minute and were integrated on an hourly basis and stored on a datalogger (CR-10x and CR-10, Campbell Scientific Inc.).

2.2.5 Diffusion through the PVDF membrane

Polyvinylidene difluoride (PVDF) is a semi-crystalline thermoplastic polymer, whose remarkable chemical and mechanical resistances make it an ideal candidate for the construction of a liquid proof barrier for flexible tubes used in chemical engineering or building construction (Briscoe *et al.* 1998). Briscoe *et al.* (1998) showed that the diffusion coefficient D ($\text{m}^2 \text{s}^{-1}$) of CO_2 through PVDF may vary approximately from 10^{-9} to $\sim 10^{-7} \text{m}^2 \text{s}^{-1}$, depending on pressure, CO_2 concentrations and the temperature.

We determined the CO_2 diffusion coefficient (D) of our PVDF membrane with a modified diaphragm-cell with two volumes, that is left (C_{left}) and right (C_{right}) chambers which were separated by a PVDF membrane (Figure 2).

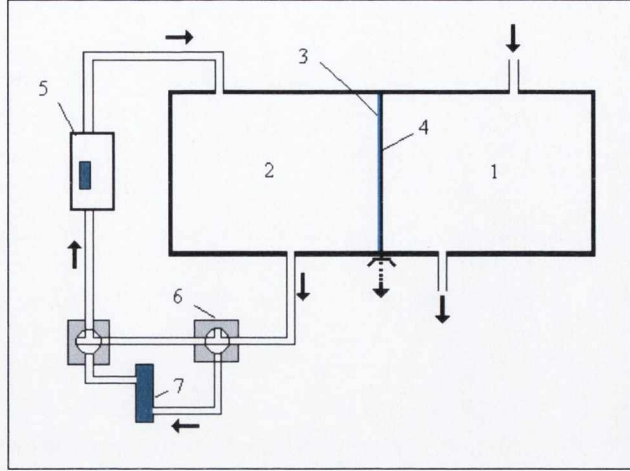


Figure 2: Schematic of the diaphragm-cell apparatus, designed to determine the CO₂ diffusion coefficient (D) of our PDVF membrane. The physical barrier (4) was kept in place until the starting point (right chamber (1) at $\approx 600 \mu\text{mol mol}^{-1}$ and left chamber (2) at $0 \mu\text{mol mol}^{-1}$) was achieved. The physical barrier was removed, by sliding out in the direction of the broken arrow, and the two valves (6) were switched off to exclude the sodalime scrubber (7). The time and the CO₂ concentration changes taken for the left chamber to reach equilibrium with the right chamber was recorded by the IRGA (5).

The two chambers were filled with gas at different CO₂ concentrations. The CO₂ concentration within C_{left} was maintained at approximately $0 \mu\text{mol mol}^{-1}$ using a soda lime scrubber, while C_{right} was filled with a CO₂ standard of known concentration ($600 \mu\text{mol mol}^{-1}$, CryoService, Worcester, UK). A physical barrier separated the gases within each chamber, this was removed and the time taken for C_{left} to reach equilibrium with C_{right} was recorded.

To calculate the CO₂ diffusion coefficient, we used the model of Zhang *et al.* (2005). This model assumes that gaseous flux across the diaphragm rapidly reaches a steady-state equilibrium and that a steady-state flux is achieved even though the CO₂ concentrations in the left and right chambers change with time. The mass balance ensures that:

$$\frac{d}{dt} \cdot (C_{\text{left}} - C_{\text{right}}) = D \cdot \beta \cdot (C_{\text{right}} - C_{\text{left}}), \quad [1]$$

where

$$\beta = \frac{AH}{L} \cdot \left(\frac{1}{V_{left}} + \frac{1}{V_{right}} \right) \quad [2]$$

In Equations (1) and (2) parameter β is a geometric parameter, set to $1.43 \times 10^{-3} \text{ m}^{-2}$ in our experiment, with A equal to approximately 53 cm^2 , the volume of the right chamber (V_{right}) is equal to infinity, as the CO_2 concentration in the gas volume is kept constant by the test CO_2 standard, and the left volume (V_{left}) is equal to 615 cm^3 . H is the partition coefficient, which has a value of 1 since the gas is presumed to be insoluble in the membrane, and L is the thickness of the PVDF membrane (0.06-0.08 mm). With this boundary conditions Equation (1) becomes

$$\frac{C_{left}}{C_{right}} = 1 - e^{-\beta Dt} \quad [3]$$

Experiment No.	Ds (m^2/s)
1	4.2
2	3.5
3	4.0
4	4.1
Average	3.95 ± 0.31

Table 1 The average diffusion coefficient of CO_2 through the PVDF membrane in the four experimental tests ($3.95 \times 10^{-8} \pm 0.31 \text{ m}^2 \text{ s}^{-1}$)

Fitting the experimental ratio C_{left}/C_{right} to Equation 3 determines the diffusion coefficient of the CO_2 , as illustrated in Figure 3. After four experimental repetitions, we found a mean diffusion coefficient of approximately $3.95 \times 10^{-8} \pm 0.31 \text{ m}^2 \text{ s}^{-1}$ (Table 1), with equilibration times t_{eq} close to 14 minutes. (Figure 3), and thus falling within the range reported by Briscoe *et al.* (1998).

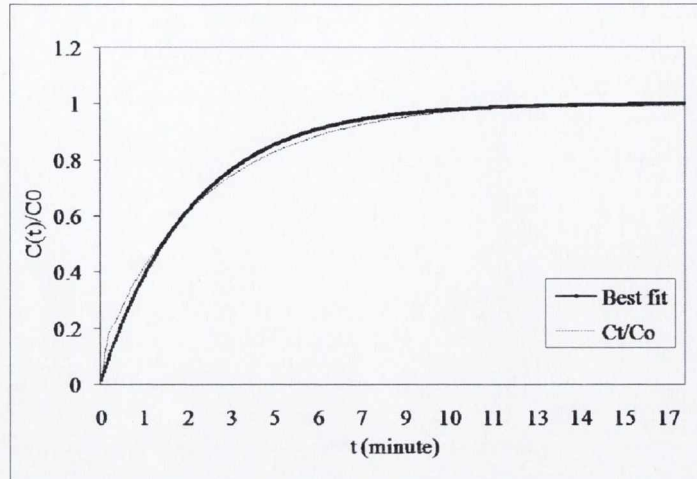


Figure 3: Diaphragm-cell result for CO₂ diffusion into the left chamber. Experimental data are fit into Eq. (3). The broken line represents the ratio of the CO₂ conc. inside the left chamber of the diaphragm-cell apparatus versus the constant CO₂ conc. of the right chamber.

2.3 Results and discussion

2.3.1 CO₂ field profile measurements

When the system had been in place for eight months, seasonal patterns of CO₂ concentrations, soil temperature and volumetric moisture content were measured from April to December 2007 at 0, 10, 20, 40 and 80 cm soil depths (Figure 4). Hourly mean CO₂ concentration from the two sites fluctuated between 416 to 1245 $\mu\text{mol mol}^{-1}$ at the soil surface, from 617 to 13030 $\mu\text{mol mol}^{-1}$ at 10 cm, and from 1768 to 23916 $\mu\text{mol mol}^{-1}$ at 20 cm. Over the same period the CO₂ concentration varied from 2097 to 24464 $\mu\text{mol mol}^{-1}$ at 40 cm and from 2960 to 23965 $\mu\text{mol mol}^{-1}$ at 80 cm.

CO₂ concentrations tended to be correlated with soil water content at all depths within the soil profile. Heavy rainfall events, which interrupt the open-air void pathway to the atmosphere, significantly affected the CO₂ concentration in the soil creating peaks of CO₂

concentration which shifted downward through the profile. During the subsequent drying process of the soil (by drainage and evapotranspiration), CO₂ concentrations decreased in a similar manner at all depths, resulting in a decline of values in prolonged dry well-aerated soil conditions (Figure 4).

Diurnal changes in soil CO₂ concentration were especially strong in the upper soil layers to a depth of 20 cm and included an early morning minimum and a late afternoon maximum, reflecting changes of soil temperature. Deeper in the soil profile the diffusion chambers at 40 and 80 cm exhibited a reduction in the diurnal amplitude of CO₂ concentration but which remained in phase with soil temperature (Figure 5).

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Diurnal changes in soil CO₂ concentration were especially strong in the upper soil layers to a depth of 20 cm. It included an early morning minimum and a late afternoon maximum, reflecting changes of soil temperature. Deeper in the soil profile the diffusion chambers at 40 and 80 cm exhibited a reduction in the diurnal amplitude of CO₂ concentration but changing CO₂ concentrations at these depths also remained in phase with soil temperature (Figure 5).

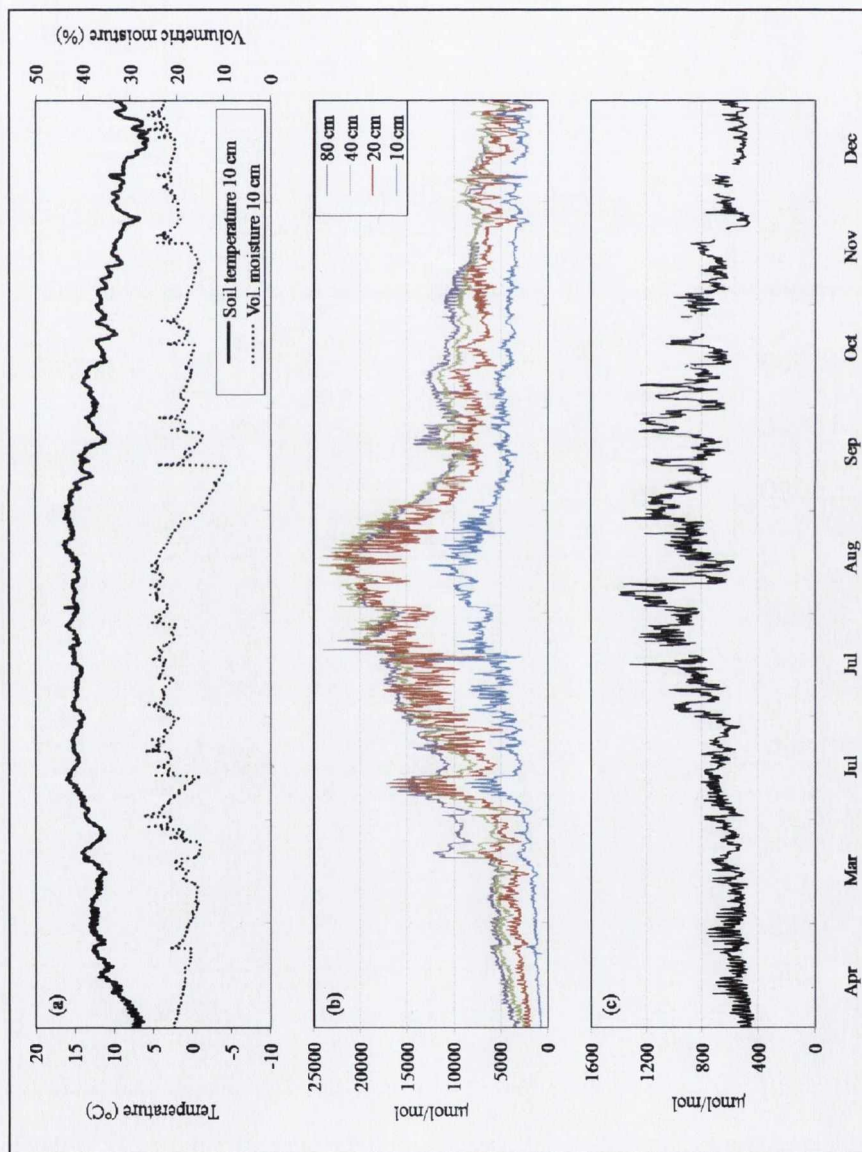


Figure 4: Seasonal patterns between April and December in 2007. (a) Soil temperature and volumetric water content at depth of 10 cm; (b) CO₂ concentration in the soil at depths of 10, 20, 40 and 80 cm; (c) CO₂ concentrations at soil surface.

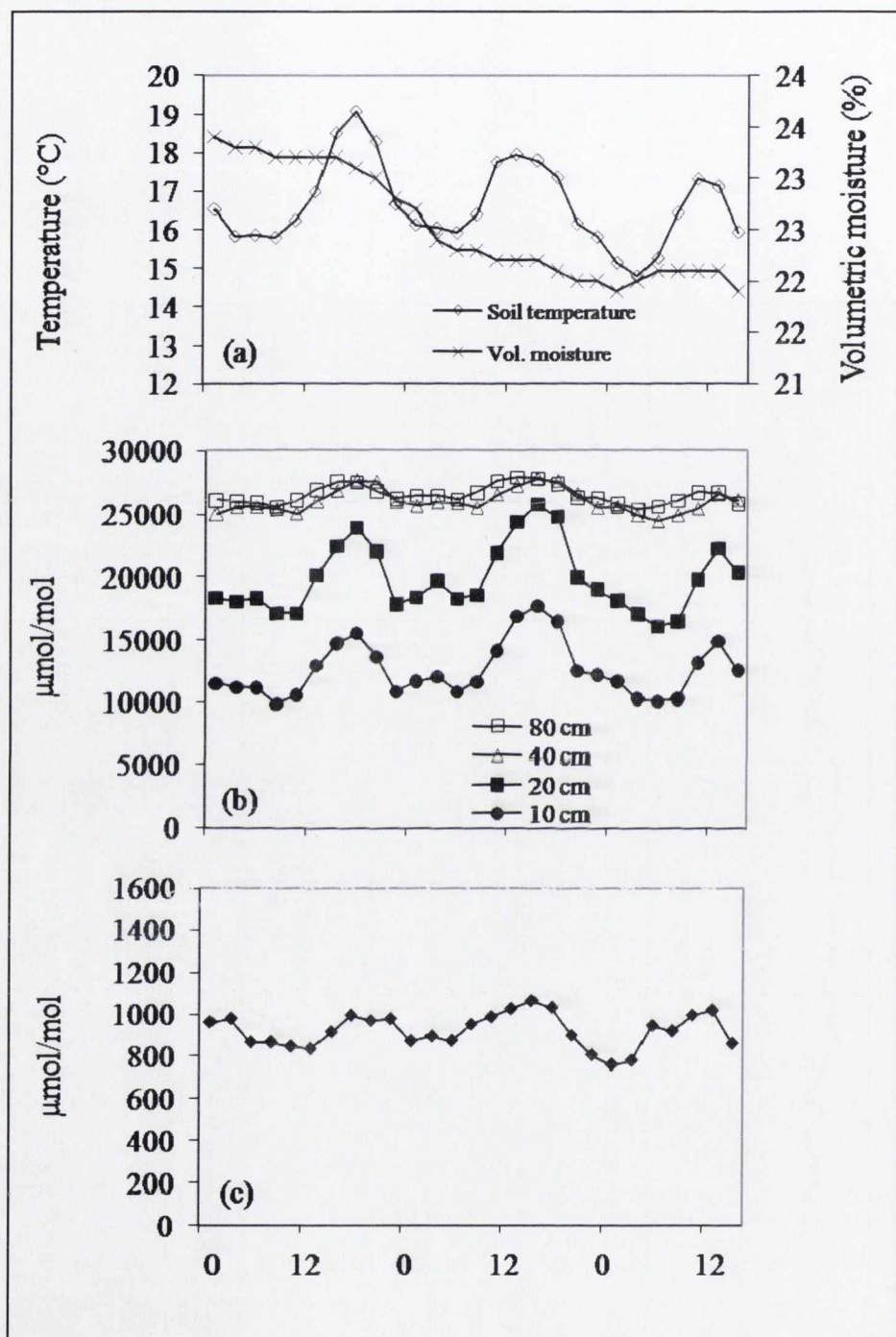


Figure 5: Temporal variation of soil CO₂ concentration in the profile from the 24th to the 26th of August 2007. (a) Soil temperature and volumetric water content at depth of 10 cm; (b) CO₂ concentration in the soil at depths of 10, 20, 40 and 80 cm; (c) CO₂ concentrations at soil surface.

2.3.2 Practical performance of the diffusion chambers

Precise measurements of CO₂ concentrations at the soil surface are essential to estimate CO₂ flux using the gradient approach. The atmospheric CO₂ concentration near the surface can be affected by advective, diffusive, and thermally induced processes and fluctuating air pressure caused by atmospheric turbulence. In previous studies, CO₂ concentrations at or near the soil surface (0-5 cm) were determined by using diffusion devices, developed to make below-ground measurements (Fang and Moncrieff, 1998; Gut *et al.*, 1998; Kamman *et al.*, 2001; Tang *et al.*, 2003; DeSutter *et al.*, 2008). However, the placement of such devices may alter the structure of the soil, thereby potentially introducing artifacts in CO₂ measurements (DeSutter *et al.*, 2008).

Here we have developed a new type of diffusion chamber to measure with accuracy CO₂ concentration near the soil surface and the use of this chamber (unpublished data) has given promising results to model the vertical gradient of CO₂ concentration along the soil profile and in a range of soil conditions.

Despite its small dimension (Figure 1), it is recommended that the surface diffusion chamber is moved periodically to avoid modification of soil moisture at the soil surface and the development of fungal growth on the surface enclosed by the chamber. Another problem associated with these measurements is the change in air temperature inside the surface diffusion chambers and the subsequent modification of the soil temperature at the surface. Because the experiment was performed under a *Miscanthus x giganteus* stand providing constant shade from the extensive above ground canopy, the small dimension of the chambers and the constant circulation of soil air achieved by the closed loop system, we assumed that

the increase in air temperature inside the surface diffusion chambers was small. However, further investigations are needed to optimize the use of the surface diffusion chambers and to avoid such problems with bare soils.

During the study period (14 months), only the soil diffusion chambers located at soil surface failed to work properly on a few occasions. After heavy rains, in July, October and November (Figure 4a), water was found in the nylon sampling tubes attached to one of the surface diffusion chambers. An investigation into the soil surface chamber design revealed that the nylon sampling tube attached to the bottom of the chamber, close to the soil surface, was drawing up water accumulated at the surface. To avoid this problem, we inserted the sample tube at a slightly higher point on the chamber.

Moreover, the equilibration time of the gas phase between the soil diffusion chamber, the multi-port solenoid valves and gas analyser depends on the length of the tubes that connects them. To reduce systematic differences between the chamber measurements, we therefore recommend using tubes of similar length at all depths. Finally, in our experiment no corrections were applied for the effect of the water vapour on the IRGA measurements of the surface chamber. However, the effect of water vapour on the CO₂ measurement in our system was small. Typically, the difference between 10% RH and 90% RH on the uncorrected CO₂ reading was 2-6 ppm. The reason for the small humidity effect is because there are two opposing processes that tend to be of equal magnitude, the dilution effect which reduces the relative number of CO₂ molecules in the mixture reducing the infrared absorption, and pressure broadening which tends to increase the absorption (PP Systems, 2003).

2.3.3 Advantages of using automated soil diffusion chambers

The results reported in this study showed that soil diffusion chambers can be a valuable technique to measure soil CO₂ concentrations within the soil profile continuously or semi-continuously and without the need for soil gas extraction. The PVDF membrane, used to construct the diffusion chambers, guarantees a good diffusivity of soil CO₂ into the chambers, which may depend on the CO₂ concentration in the soil.

To measure accurately short-term variation in soil CO₂ concentrations, we need sampling systems with fast equilibration times (Fang and Moncrieff, 1998). Considering the flow rate used in our system (50 ml minute⁻¹), the volume of the closed loop (100 cm³) and the volume of the chamber (365 cm³), the gas is circulated approximately three times during the 30-minute measuring period. In our preliminary experiment to test the CO₂ diffusivity through the PVDF membrane, we found CO₂ concentration equilibrium time of 14 minutes (Figure 3). Based on these results, and the fact that the ratio chamber volume/diffusion area in our field experiment was approximately 50% smaller than in our preliminary experiment, we are confident that equilibrium times in our sampling system are less than 14 minutes.

The closed gas circuit used in this experiment has the major advantage that it limits the creation of pressure differentials within the diffusion chamber, and between the diffusion chamber and the surrounding soil. In addition, by using the gas permeable PVDF membrane, to separate the soil/water from the gas phase, we avoid the probability of mass gaseous flow in the soil matrix from undefined depths.

The accuracy of measuring the movement of CO₂ throughout the soil profile allows us to use the diffusion chamber system to provide additional information on the transport of the CO₂

in the soil profile in relation to temperature, water content and gas diffusivity. Promising results were obtained by use of the soil diffusion chamber (unpublished data) to calculate vertical production rates within the soil profile and to estimate soil surface CO₂ fluxes.

This profile diffusion system can be used in wet, even waterlogged, soil conditions, because the PVDF membrane excludes H₂O whilst allowing CO₂ to diffuse across the chamber membrane. The inclusion of a metal and plastic mesh provides physical protection from micro and macrofauna while maintaining the diffusion properties of the PVDF membrane. Moreover, the PVDF membrane inhibits bacterial attachment and biofilm formation (Yabune *et al.*, 2005).

Additional advantages of the soil diffusion chambers used in this study are that they are inexpensive to construct and do not require essential maintenance work; once installed they can be used in long-term field studies. Finally, their small dimensions have the advantage of reducing the initial disturbance of the soil at installation.

Chapter 3

Soil respiration using soil diffusion chambers: a gradient-based study approach

Summary

To better understand the various processes governing the CO₂ exchange within the soil, high-temporal resolution CO₂ concentrations in soil pore space were monitored under *Miscanthus × giganteus* by automated diffusion chambers, and used to estimate gradient-based soil CO₂ efflux. Characterized by a quadratic shape along the five measuring points of the soil profile, the CO₂ concentration gradient varied in phase diurnally, weekly, and seasonally with soil temperature, volumetric water content, atmospheric pressure and wind speed. With the start of the growing season the CO₂ efflux showed an apparent differential response to soil warming and cooling which led to a pronounced diurnal hysteresis effect. Furthermore, a phase shift between the daily peaks of CO₂ efflux and soil temperature increased during the growing season reaching a maximum time lag of approximately three hours in June. The soil respiration-temperature relationship described by Q_{10} varied from 4.3 to 7.6 throughout the soil profile, showing better R^2 values when soil temperature measured between 10 and 40 cm depth was considered. Efflux calculated from soil CO₂ concentration gradient closely agreed with surface chamber efflux measurements, highlighting the accuracy of automated diffusion

chamber on measuring CO₂ concentration not only at soil surface, but also within the soil profile.

3.1 Introduction

In the last two decades much research has been dedicated to study the role of the terrestrial biosphere as a global carbon source or sink. CO₂ emission from soil as respiration is the major pathway by which soil organic carbon moves from the soil to the atmosphere (Schlesinger et al. 2007). Measuring and predicting soil respiration can be challenging because the CO₂ efflux from soil integrates several complex below-ground processes and fluxes, such as respiration by roots, mycorrhizae, rhizosphere, and saprophytic microbes.

Researchers have predominantly focused on the measurement of fluxes at the soil surface. Manual and automated soil surface chambers provide an easy, efficient, and reliable method to measure CO₂ efflux at the soil surface, and to capture its spatial variability from almost any type of landscape. However, soil respiration varies with depth, as do the environmental factors that regulate it. Therefore, it is important to enhance our understanding of the various processes of production and transport of CO₂ in soil, and how these processes are affected by changes in environment and soil variables.

Measuring vertical profile of CO₂ efflux can be challenging. Beside the need to develop novel techniques for reliable measurements of belowground CO₂ concentration gradient, there is the difficulty of estimating the soil CO₂ diffusion coefficient. However, despite these difficulties, numerous approaches to soil profile measurement have been carried out. Initially several manual sampling techniques of measuring belowground CO₂ concentrations were

developed. This included capillary tubes (Hack, 1956; Tackett, 1968; Roulier *et al.*, 1974, Burton and Beauchamp, 1994, Sotomayor and Rice, 1999, Goodroad and Keeney, 1985, Cates and Keeney, 1987), diffusion probes (Taylor and Abrahams, 1953, Patrick, 1977), gas traps (Fang and Moncrieff, 1998), gas permeable tubes (Holter, 1990 Jacinthe and Dick, 1996; Nielsen *et al.*, 1997; Kammann *et al.*, 2001), and gas permeable membranes probes (Kasparov *et al.*, 1985; Panikov *et al.*, 1993). More recently researchers have taken advantage of the opportunity to measure short-term changes in belowground CO₂ concentration (Hirano *et al.*, 2000; Tang *et al.*, 2003; Jassal *et al.*, 2005) using industrial solid-state CO₂ sensors, developed primarily for air quality monitoring and control, installed at different soil depths. Others have developed automated systems for continuous measurements of soil gases (Gut *et al.*, 1998; Flechard *et al.*, 2006, Panikov *et al.*, 2007, DeSutter *et al.*, 2008), by combining techniques such as gas permeable tubes or permeable probes with infrared gas analyzers, and solid-state CO₂ sensors. Although there are numerous shortcomings associated with the above techniques, all these studies have contributed to better understand the belowground dynamics of CO₂ production and transport.

Recently Albanito *et al.* (2009) have described a new type of automated soil diffusion chambers which permits high-temporal resolution of soil profile CO₂ concentration measurements, as well as the possibility of carrying out long term field experiments in dry, wet or even waterlogged soil conditions. Using these data the objectives of this study were: (i) to calculate the high temporal resolution CO₂ efflux using a site-specific gradient-based model, (ii) to report diurnal and seasonal variation of CO₂ effluxes, (iii) to compare and examine estimated gradient-based CO₂ efflux and measured surface CO₂ efflux, (iv) to explor

high temporal resolution diel patterns of CO₂ efflux related to soil temperature, soil moisture and other environmental parameters.

3.2 Material and methods

3.2.1 Site description

Measurements were carried out throughout 2008 in a 14 year old *Miscanthus x giganteus* stand located at the Teagasc (Irish Agricultural Research Institute), Crops Research Centre, Oak Park, Carlow (52° 51' N, 6° 54' W, 50 m above sea level). The climate is Oceanic with no extremes of temperature. The mean annual air temperature at the site in 2008 was about 9.7 °C with summer mean daily maximum of about 19 °C and winter mean daily minimum is about 2.5 °C. The annual number of days with more than 1 mm of rain was about 180, and the average annual rainfall was about 1000 mm (Figure 1).

As described in Chapter 3.2, the soil of the *Miscanthus x giganteus* stand (Table 1) was classified, following the classification scheme for England and Wales (Avery, 1980), as a brown podzolic soil. Analysis of total soil organic carbon (*TOC*) and total nitrogen (*N*) were performed by elemental analysis (LECO), whereas the soil particle density (*PDs*) was measured by submersion method (ASTM, 1992a). Finally, total bulk density (*D_b*) for each soil profile depth was determined using intact soil cores extracted manually from the soil profile. By drying each soil core in oven at 60 degrees for up to 7 days, and storing at room temperature for 2–4 weeks to redistribute the soil water content, each core was weighed, and

successively tightly wrapped in polyethylene sheet to determine the volume by water displacement method.

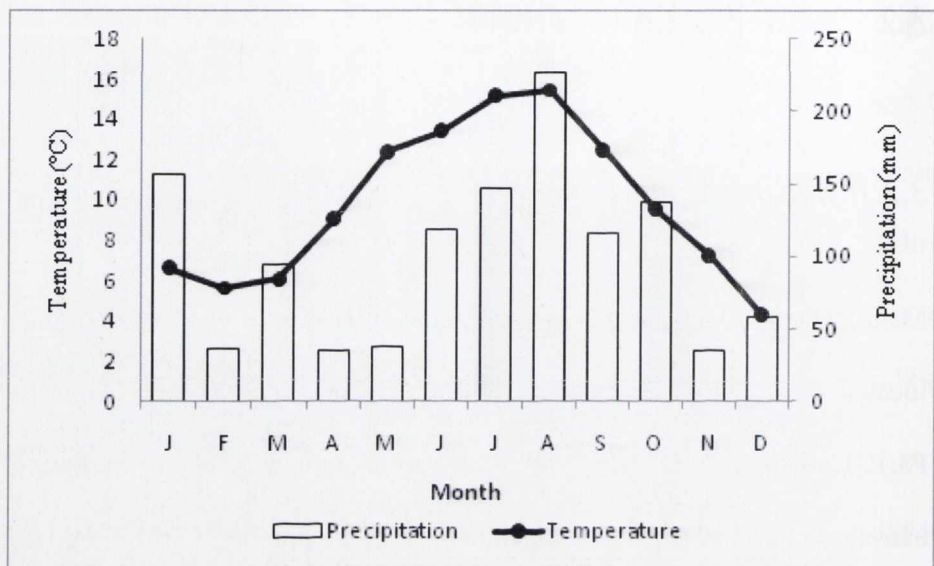


Figure 1: Monthly mean values of air temperature and rainfall for the year 2008 at the Teagasc Irish Agricultural Research Institute Oak Park, Crops Research Centre, Carlow, Ireland (52° 51' N, 6° 54' W, 50 m asl)

3.2.2 Measurements of CO₂ concentrations and soil parameters

Carbon dioxide concentration in the soil profile was monitored using the soil diffusion chamber technique (see Chapter 2). In essence, one surface diffusion chamber and four soil diffusion chambers were placed at depths of 0, 10, 20, 40 and 80 cm in the soil. Both the surface and the soil diffusion chambers were connected by a pair of nylon sampling tubes, with inner and outer diameter of 0.4 and 0.6 cm respectively, to a multi-port valve system (ACL s.r.l, 20040 Cavenago di Brianza, Milan, ITALY), which feeds the gas sample into an infra red gas analyzer (Environmental gas monitor WMA-2; PP Systems Hitchin,

Hertfordshire UK) with a flow rate of 50 ml min^{-1} . The output signals of the gas analyzers were collected every second, integrated over a period of 5 minutes, and stored on a datalogger (21-X, Campbell Scientific Inc.). The multi-port solenoid system performed a daily routine of nine sub-cycles measurements. Each sub-cycle measurement of 150 minutes allowed the sequential measurement of all five chamber depths for a duration of 30 minutes. For further technical details of this technique see Albanito et al. (2009).

Alongside the chambers at depths of 0, 10, 20, 40, 80 cm, soil volumetric water content and soil temperature were measured continuously using dielectric sensors (ECH2O EC-5 Decagon Devices, Inc., 950 NE Nelson Court, Pullman, WA, USA) and custom-manufactured Cu-Constantan thermocouples. Hourly measurements of precipitation were obtained using a tipping bucket rain gauge (Model ARG100, Campbell Scientific Ltd, Leicestershire, UK) and horizontal wind speed and direction was measured using a vane anemometer (Model 05103, R.M. Young Co., Traverse City, MI, USA) positioned 2 m above the soil surface.

Output signals from the soil moisture probes, thermocouples, rain gauge, and anemometer, were recorded every minute and were integrated on an hourly basis and stored on a datalogger (CR-10x and CR-10, Campbell Scientific Inc.).

Finally, soil CO_2 efflux was also measured using an automated efflux chamber (ACE System, ADC BioScientific Ltd, UK). The soil collar of the automated chamber of 5 cm height and 23 cm diameter was inserted into the soil a depth of 3 cm in close proximity to the soil profile CO_2 gradient system. Soil CO_2 flux was measured every 30 minutes and integrated to 150 minute averaged values.

3.2.3 Calculation of gradient-based CO₂ efflux

The calculation of the soil CO₂ efflux was derived using the Fick's first law:

$$F = -D_s \frac{dC}{dz} \approx -D_s \frac{\Delta C}{\Delta Z} \quad [1]$$

where F is the flux of CO₂ ($\mu\text{mol m}^{-2} \text{s}^{-1}$), D_s is the soil diffusion coefficient of CO₂ in the soil ($\text{m}^2 \text{s}^{-1}$) (discussed in more detail below), C is the concentration of CO₂ ($\mu\text{mol m}^{-3}$), and z is the depth below the soil surface (m). $\Delta C/\Delta Z$ is the gradient of CO₂ concentration ($\mu\text{mol m}^{-3}$) at each depth, and it is obtained conducting a non linear regression analysis on the CO₂ concentrations ($\mu\text{mol mol}^{-1}$) measured across the soil profile

3.2.4 Calculation of the soil CO₂ diffusion coefficient

Although several models have been used to describe the relationship between the relative gas diffusion coefficient in soil, porosity and soil moisture (Penman, 1940; Marshall, 1959; Millington-Quirk, 1961; Moldrup et al., 1999), the soil CO₂ diffusion coefficient (D) in our site was estimated adopting the Millington and Quirk model (Millington and Quirk, 1961):

$$\frac{D_s}{D_a} = \xi \quad [2]$$

where D_a is the CO₂ diffusion coefficient in the free air, $\xi = \frac{\varepsilon^{10}}{\phi^2}$ is the gas tortuosity factor (Jury et al., 1991), ε is the soil air-filled porosity, and ϕ is the total porosity ($\text{m}^3 \text{m}^{-3}$) calculated by the following equation:

$$\phi = \left(1 - \frac{D_b}{PD_s}\right) \times 100 \quad [3]$$

where D_b (g cm^{-3}) is the bulk density, and PD_s (g ml^{-1}) is the particle density of the soil within each soil layer.

To account for the spatial variation in texture properties of the soil profile, and non uniform vertical distribution of soil water content, we calculated the effective diffusion coefficient (D_s) based on harmonic averaging of individual diffusivities of each profile layer, therefore resembling the slope of a linear regression between the individual D_s of each layer and the soil depth:

$$D_s = \frac{\sum_{k=1}^n \Delta Z_k}{\sum_{k=1}^n \frac{\Delta Z_k}{D_{sk}}} \quad [4]$$

where D_{sk} represents the soil CO_2 diffusion coefficient for a discrete layer k .

3.2.5 Data analysis

The quadratic model of the CO_2 concentration gradient was developed using MATLAB (MatWorks Inc., Natick, Massachusetts). The seasonal temperature sensitivity of the estimated soil CO_2 efflux at soil surface was assessed fitting the daily mean CO_2 efflux values using the van 't Hoff expression:

$$SR = R_{10} \cdot Q_{10}^{\left(\frac{T-10}{10}\right)} \quad [5]$$

where SR is the soil respiration efflux, R_{10} is the simulated soil respiration at a temperature of 10 °C, Q_{10} is the change in respiration resulting from a 10°C increase in temperature, and T is the daily mean value of soil temperature measured at 10 cm depth. Finally, the multi regression analysis on the dataset was performed with SPSS 16.0 statistical package (SPSS Inc., Chicago, Illinois).

3.3 Results

3.3.1 Soil profile characteristics

The soil profile at the site was examined from the soil surface down to the bedrock and two well developed soil horizons were identified. After an *O* horizon of about 2-3 cm thickness with a litter layer of plant residues in relatively undecomposed form, a sandy silt loam *A* horizon was identified up to a depth of 35 cm, and a sand with gravel *Bh* horizon was identified from a depth of 30 cm down to the bedrock at about 100 cm. Throughout the soil profile total organic carbon (*TOC*) varied from 43.1 g kg to 10.1 g kg, while the total nitrogen (*N*) varied from 36 g kg to 7.3 g kg. The mean particle density (*PDs*) varied from 2.34 to 2.58 g ml⁻¹, and finally the total bulk density (D_b) varied from 1.07 g cm⁻³ in the 0-10 cm layer to 1.54 g cm⁻³ (Table 1).

3.3.2 Soil profile CO₂ concentration gradient

Figure 2 shows a diurnal trend of the CO₂ concentration, soil CO₂ diffusion coefficient, soil temperature, and soil water content from the soil surface to 80 cm depth. The curve-fitting approach used to describe the curvilinear CO₂ vertical concentration gradient was computed by using a non linear regression on the CO₂ concentrations measured across the 5 soil profile depths. Because the CO₂ concentration gradient maintained a characteristic curvilinear pattern with depth the best fit was given by a quadratic model (figure 3, 4):

$$C_z = \alpha + \beta Z + \gamma Z^2 \quad [6]$$

where C_z represent the CO₂ concentration at depth Z (cm). Minimizing the sum of squares of errors for the data: 0 cm: (C_1, Z_1); 10 cm: (C_2, Z_2); 20 cm: (C_3, Z_3); 40 cm: (C_4, Z_4); 80 cm: (C_5, Z_5)

$$S = \sum (\alpha + \beta Z + \gamma Z^2) \quad [7]$$

Parameters α, β, γ are determined by least square method (standard regression). By setting these equal to zero and performing some algebra:

$$\frac{\Delta C}{\Delta Z} = \beta + 2\gamma Z \quad \text{if } Z = 0 \quad \frac{\Delta C}{\Delta Z} = \beta \quad [8]$$

<i>Layer</i> (cm)	<i>Horizon</i>	<i>Description</i>	<i>pH</i> mean $\pm$ SE	<i>TOC</i> (g kg ⁻¹) mean $\pm$ SE	<i>N</i> (g kg ⁻¹) mean $\pm$ SE	<i>PDs</i> (g ml ⁻¹) mean $\pm$ SE	<i>D_b</i> (g cm ⁻³) mean $\pm$ SE
0-10	<i>O-A</i>	Silt Loam	6.1 $\pm$ 0.06	43.1 $\pm$ 1.4	36.0 $\pm$ 1.4	2.34 $\pm$ 0.02	1.07 $\pm$ 0.05
10-20	<i>A</i>	Silt Loam	5.9 $\pm$ 0.01	43.4 $\pm$ 2.3	43.9 $\pm$ 0.8	2.38 $\pm$ 0.01	1.23 $\pm$ 0.06
20-30	<i>A</i>	Silt Loam	6.3 $\pm$ 0.05	29.0 $\pm$ 1.9	29.0 $\pm$ 1.2	2.38 $\pm$ 0.02	1.24 $\pm$ 0.07
30-40	<i>Bh</i>	Sand gravel+stones	6.1 $\pm$ 0.01	19.7 $\pm$ 2.4	21.0 $\pm$ 0.8	2.44 $\pm$ 0.04	1.27 $\pm$ 0.08
40-50	<i>Bh</i>	Sand gravel+stones	6.3 $\pm$ 0.08	8.60 $\pm$ 1.7	10.1 $\pm$ 1.1	2.49 $\pm$ 0.02	1.31 $\pm$ 0.05
50-60	<i>Bh</i>	Sand gravel+stones	6.7 $\pm$ 0.00	7.40 $\pm$ 2.2	9.5 $\pm$ 0.67	2.55 $\pm$ 0.02	1.43 $\pm$ 0.03
60-70	<i>Bh</i>	Sand gravel+stones	6.5 $\pm$ 0.04	8.30 $\pm$ 3.2	6.6 $\pm$ 0.55	2.56 $\pm$ 0.03	1.48 $\pm$ 0.03
70-80	<i>Bh</i>	Sand gravel+stones	6.5 $\pm$ 0.01	10.1 $\pm$ 2.5	7.3 $\pm$ 0.43	2.58 $\pm$ 0.01	1.54 $\pm$ 0.04

Table 1: Soil profile characteristic at the Carlow site. The brown podzolic soil profile from 0 to 80 cm depth was characterized by three horizons and described as Silt Loam from soil surface to 30 cm depth, and sand, gravel, and stones from 30 to the bedrock. Mean values of pH, total organic carbon (TOC), total nitrogen (N), particle density (PDs) and bulk density (*D_b*) are reported with the standard error (SE).

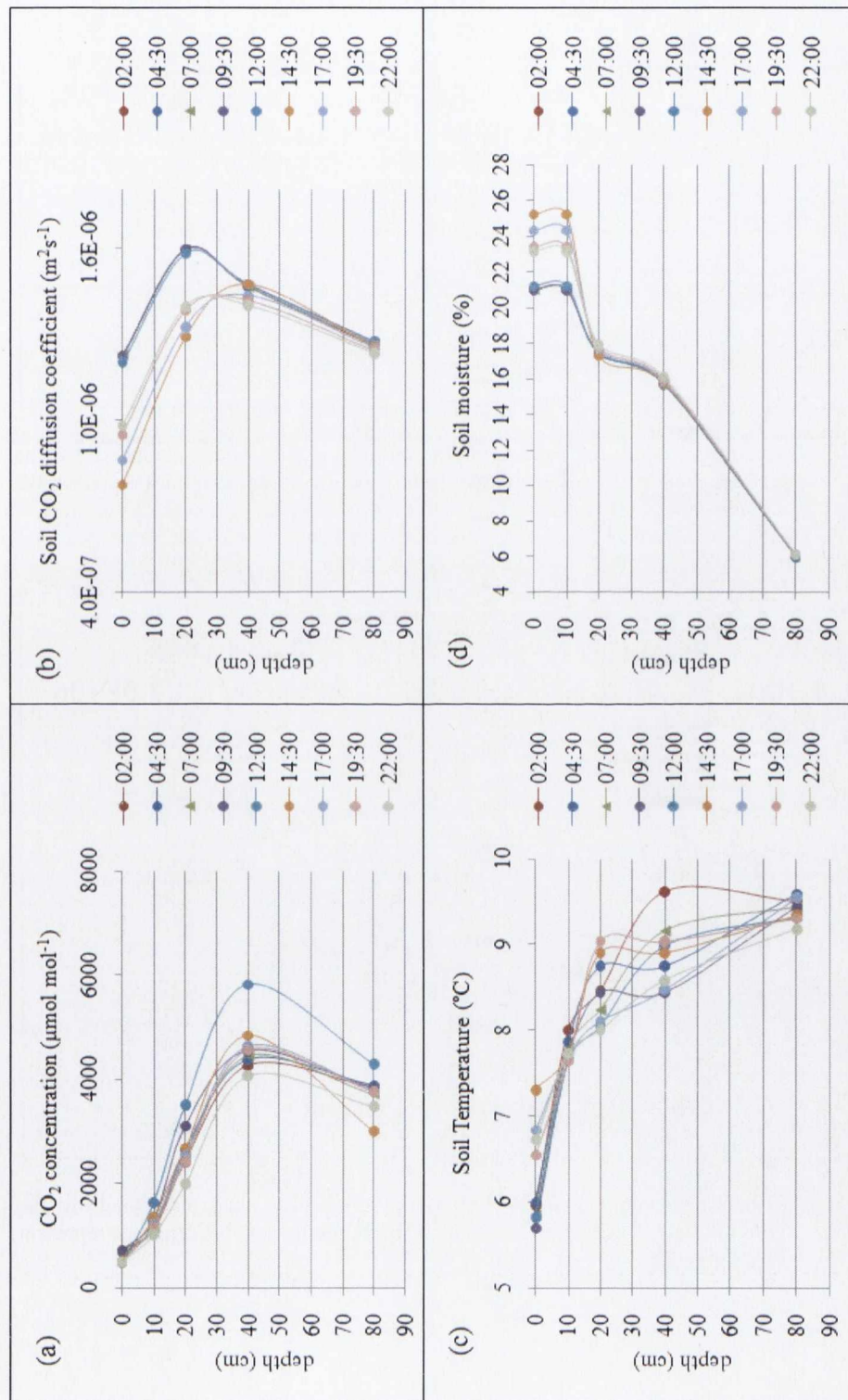


Figure 2: Diurnal trends measured from soil surface to 80 cm depth on the 4th of January of 2008: (a) CO₂ concentrations, (b) soil CO₂ diffusion coefficient, (c) soil temperature, and (d) soil water content..

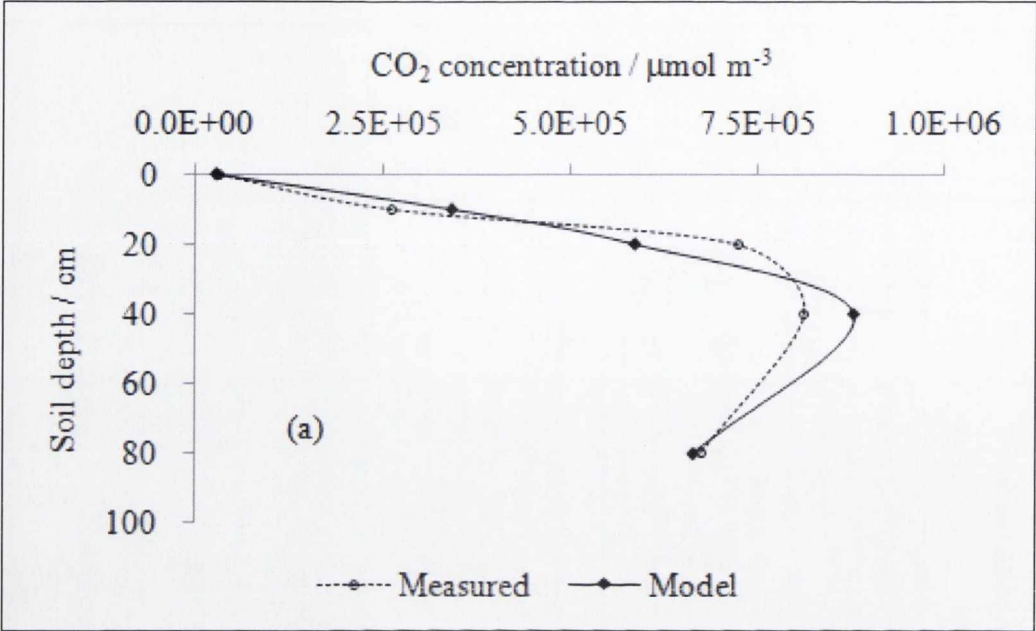


Figure 3: CO₂ concentrations measured within the soil profile, and calculated by the quadratic model, at noon on the 22nd of August 2008. The continuous and broken lines represent the quadratic curve fitted to the data.

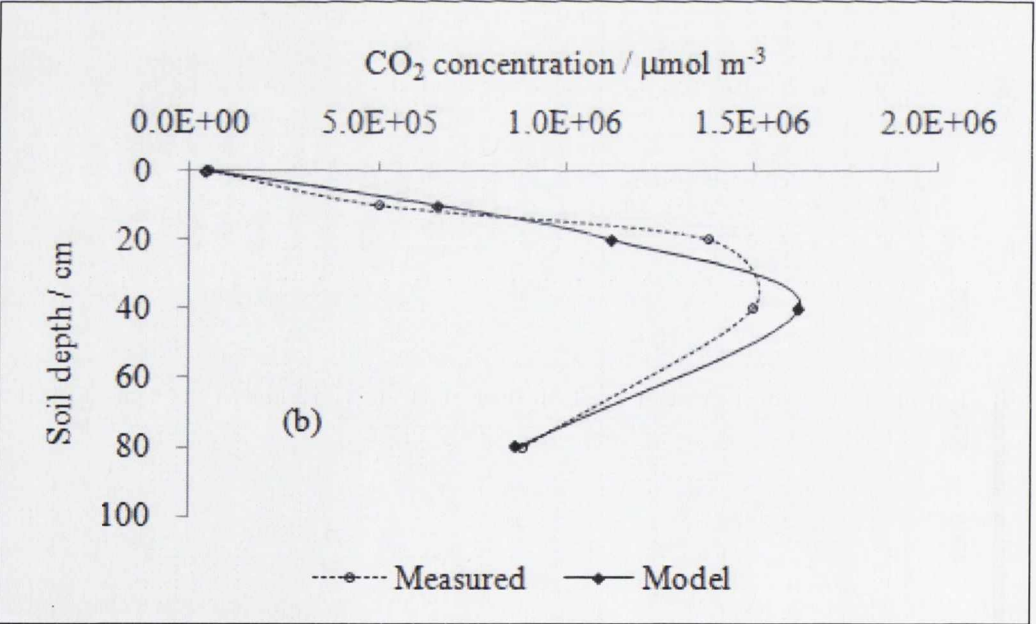


Figure 4: CO₂ concentrations measured within the soil profile, and calculated by the quadratic model, at noon on the 11th of September 2008. The continuous and broken lines represent the quadratic curve fitted to the data.

3.3.3 Diurnal pattern of soil respiration

Diurnal changes in soil CO₂ efflux showed a close relationship with soil temperature, with a morning minimum and a late afternoon maximum. Figure 5 shows diurnal variation of soil temperature and volumetric water content at a depth of 10 cm, and soil surface CO₂ efflux from the 6th to the 29th of May 2008. During the days, with dry weather condition, the soil temperature explained about the 50% of the soil CO₂ efflux variability, while no apparent correlation was found with soil water content measured at 10 cm depth.

The relationship between soil CO₂ efflux and temperature at 10 cm depth viewed in aggregate appeared to be disorganized (Figure 6). However, by highlighting diurnal patterns of CO₂ efflux it was possible to see a superposition of daily loops which became more pronounced during the growing season (from March to June 2008). This distinct pattern of hysteresis was due to a differential response of soil respiration to the daily soil warming and cooling which affected the correlation (R^2) between soil respiration and soil temperature (Figure 7). The increasing in magnitude of the hysteresis loops during the growing season can be explained as a result of the modulation of the CO₂ efflux from the autotrophic and heterotrophic respiration during the growing season. However, within the hysteresis patterns of soil respiration, the daily loop of soil respiration showed also an increasing time lag between the daily peaks of CO₂ efflux and the peaks of soil temperature, which tended to increase during the growing season (Figure 7).

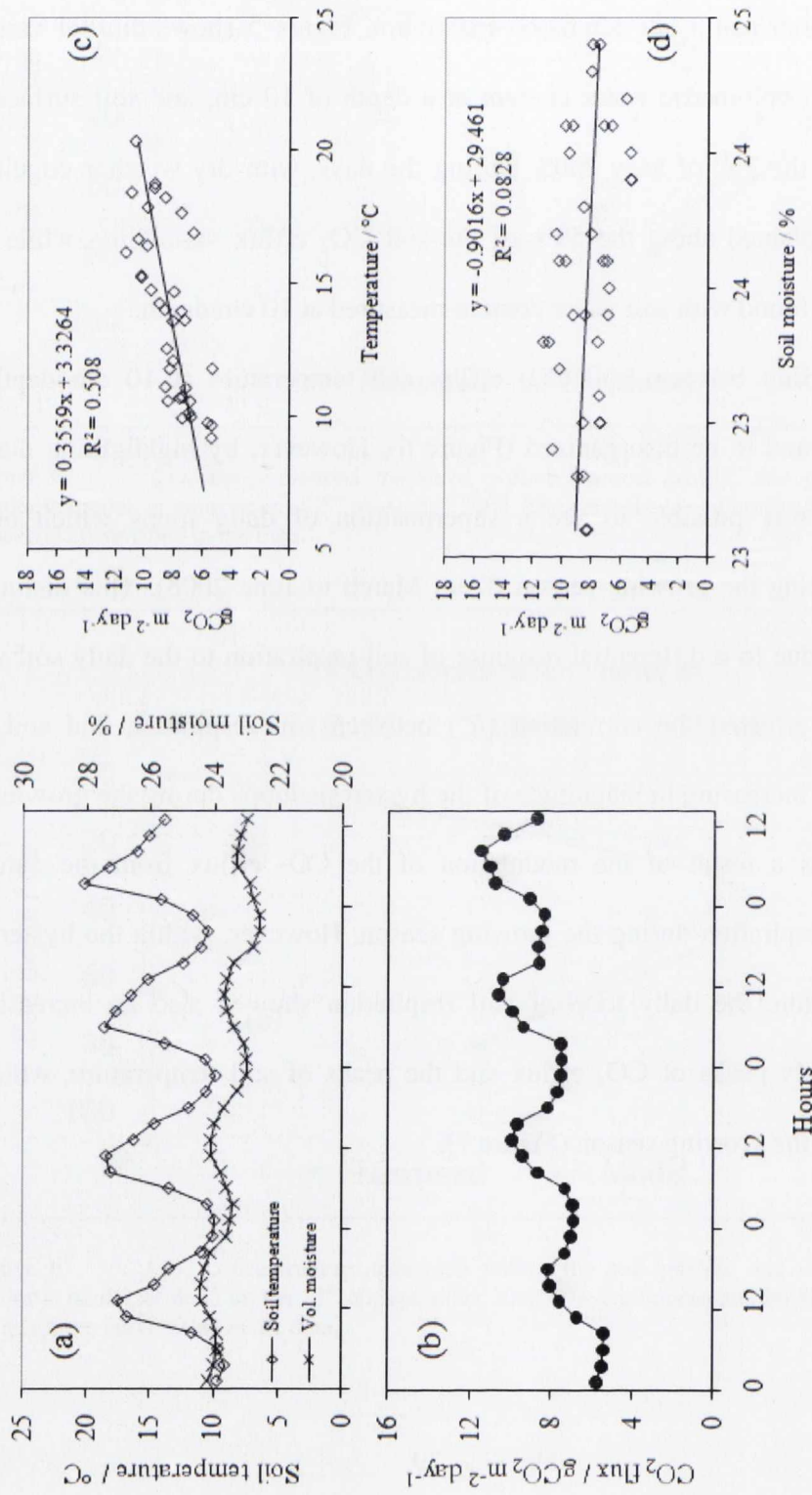


Figure 5: Influence of soil temperature and soil water content on the diurnal patterns from the 6th to the 9th of May 2008. (a) hourly mean values of soil temperature and soil moisture at depth of 10 cm, (b) hourly mean values of estimated soil respiration, (c) correlation between soil respiration and soil temperature, and (d) between soil respiration and soil moisture.

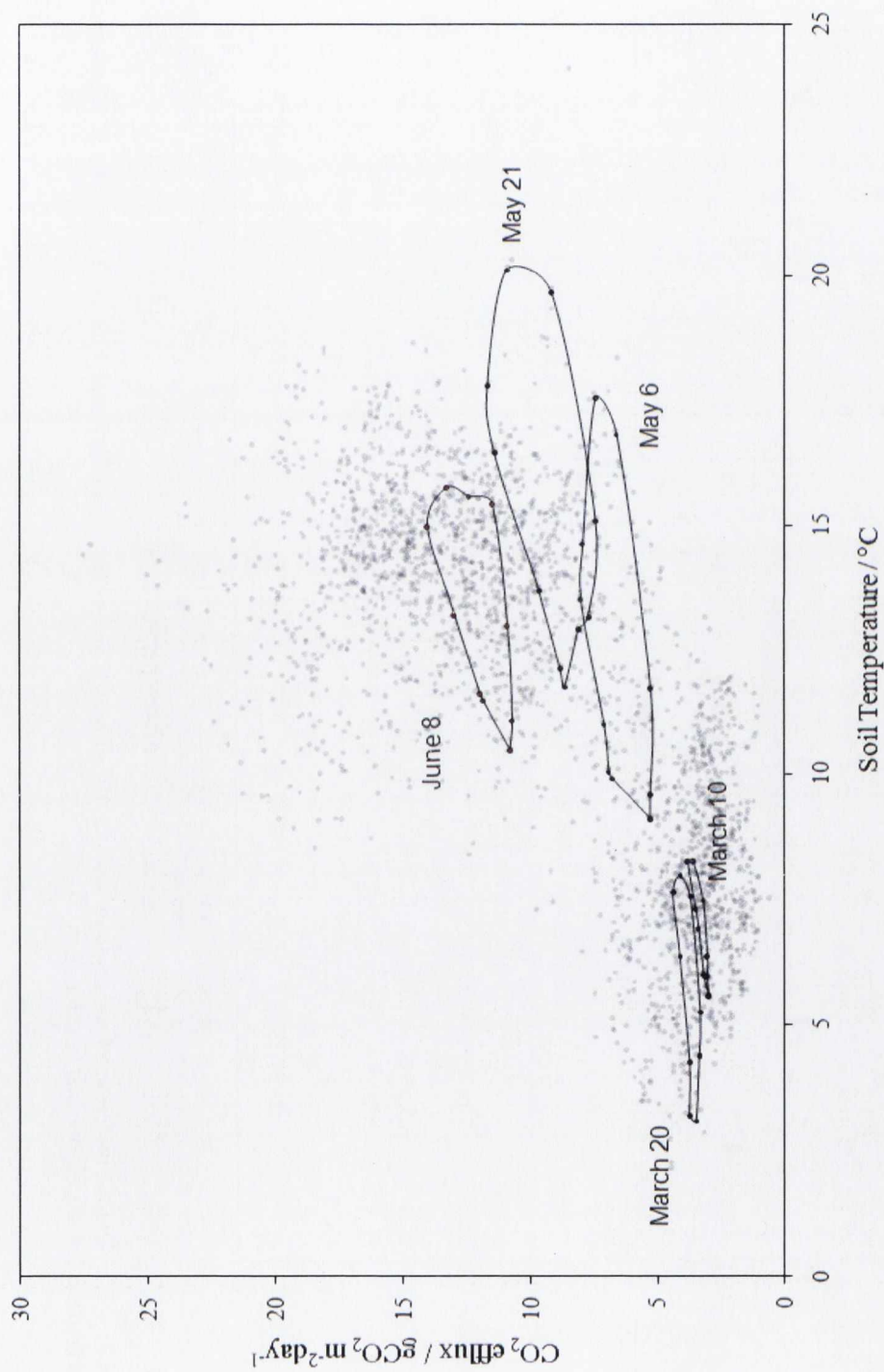


Figure 6: Mean values of estimated soil respiration vs. soil temperature at 10 cm depth from the 1st of January to the 10th of October 2008. Highlighted are hysteresis diurnal patterns of soil respiration from the 10th of March to the 8th of Jun.

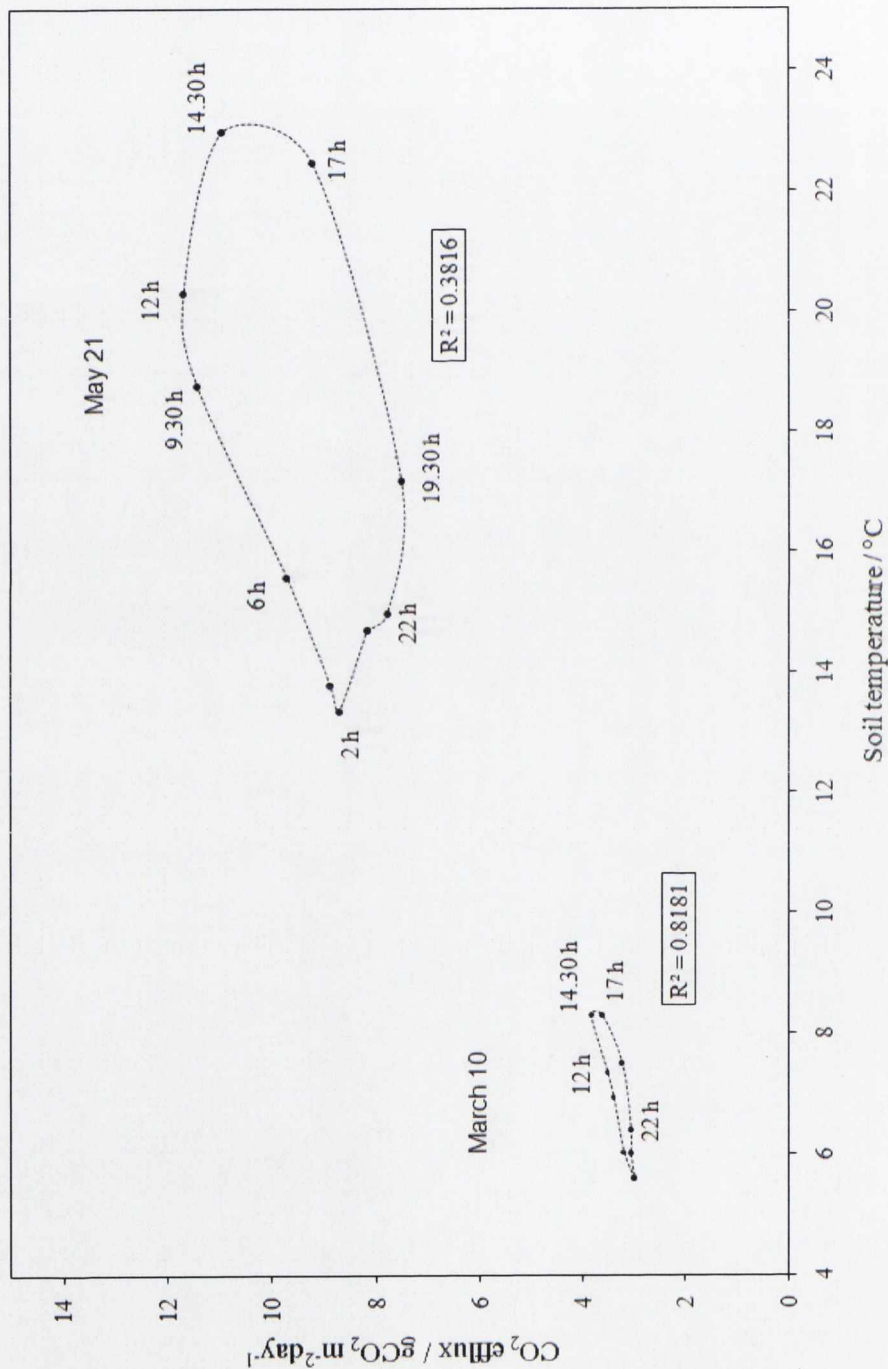


Figure 7: Diurnal hysteresis of soil respiration on the 10th of March, and on the 21th of May, with time of the day. The R^2 values were derived by fitting to the date the exponential function [Eqn. 5].

3.3.4 Weekly patterns of soil respiration

The weekly patterns of soil respiration were generally affected by synoptic weather changes associated to phases of periods of clear sunny sky, overcast, or rainy condition. As a result, this changeable condition altered the soil temperature, the humidity of the soil as well as the components of soil respiration. Figure 8 shows temporal variation of CO₂ efflux, soil temperature and soil water content at 10 cm depth from the 28th of April to the 12th of May 2008. Here, soil respiration showed not only a lower correlation to soil temperature ($R^2=0.4$) than at daily basis ($R^2=0.5$), but also a lower correlation to soil moisture, which was already negligible on a daily basis. This was due to the effect of stochastic events of rainfall which strongly increased the variability of the soil water content in the field (Figure 8b), resulting in a strong variation in soil respiration.

When synoptic weather changes were associated with severe changes of atmospheric pressure and wind conditions the CO₂ efflux in our site showed distinctive patterns driven primarily by wind speed and atmospheric pressure, with an $R^2=0.58$ and 0.54 respectively (Figure 9). The combination of rapid changes of atmospheric pressure and wind speed occurred between the 9th and 13th of September (DOY 252-256), combined with 5.2 mm of rain falling approximately 2 hours before the peak event of the 11th of September (between 12 am and 1 pm), led the CO₂ efflux patterns to vary from 10 to 27.1 gCO₂ m² day⁻¹.

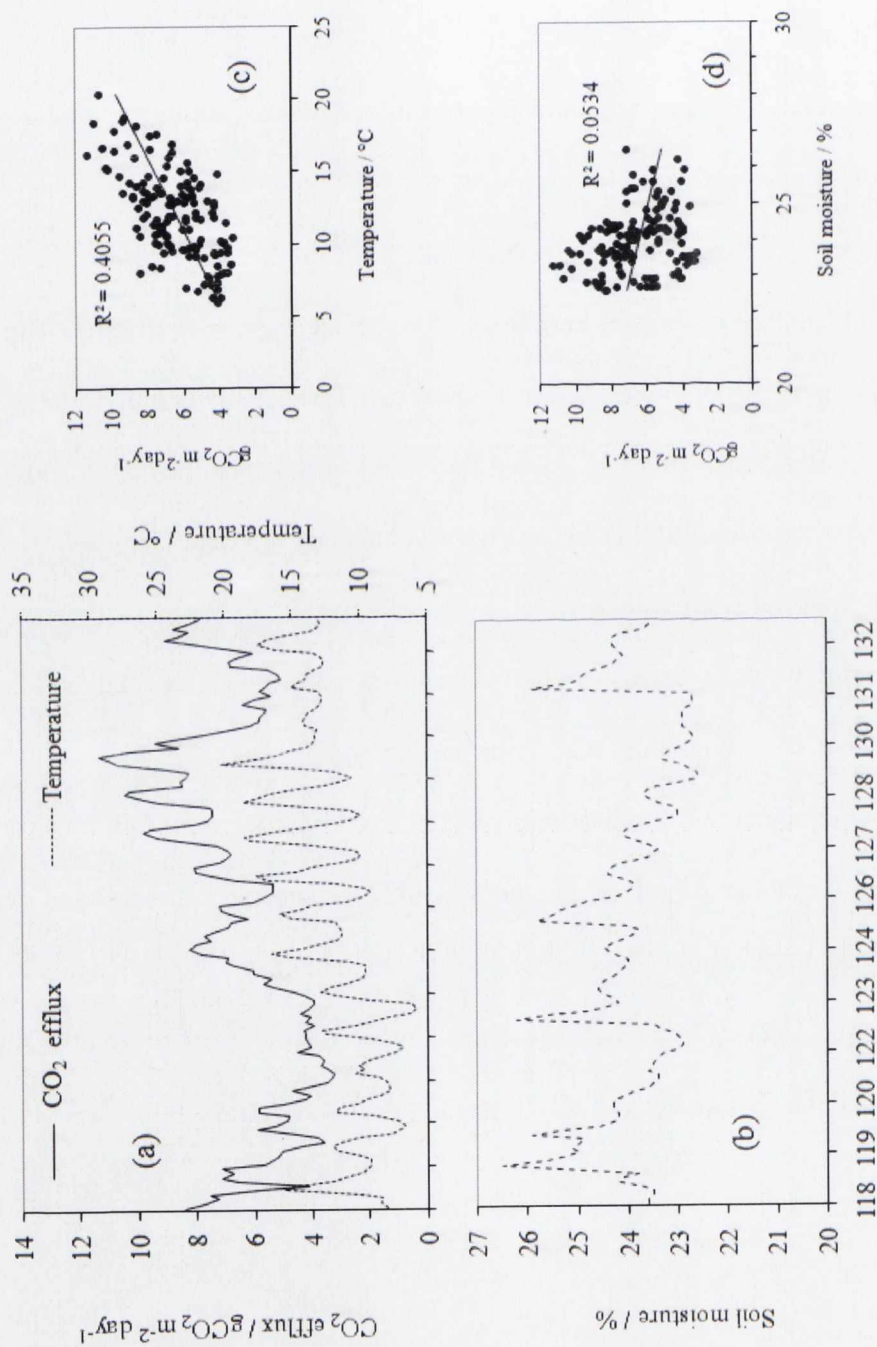


Figure 8: Influence of soil temperature and soil moisture on weekly patterns of soil CO₂ efflux from the 28th of April to the 12th of May. (a) Hourly mean soil respiration and soil temperature at 10 cm depth, and (b) soil moisture at 10 cm depth. On the right (c) relationship between soil respiration and temperature, and (d) soil respiration vs. soil moisture

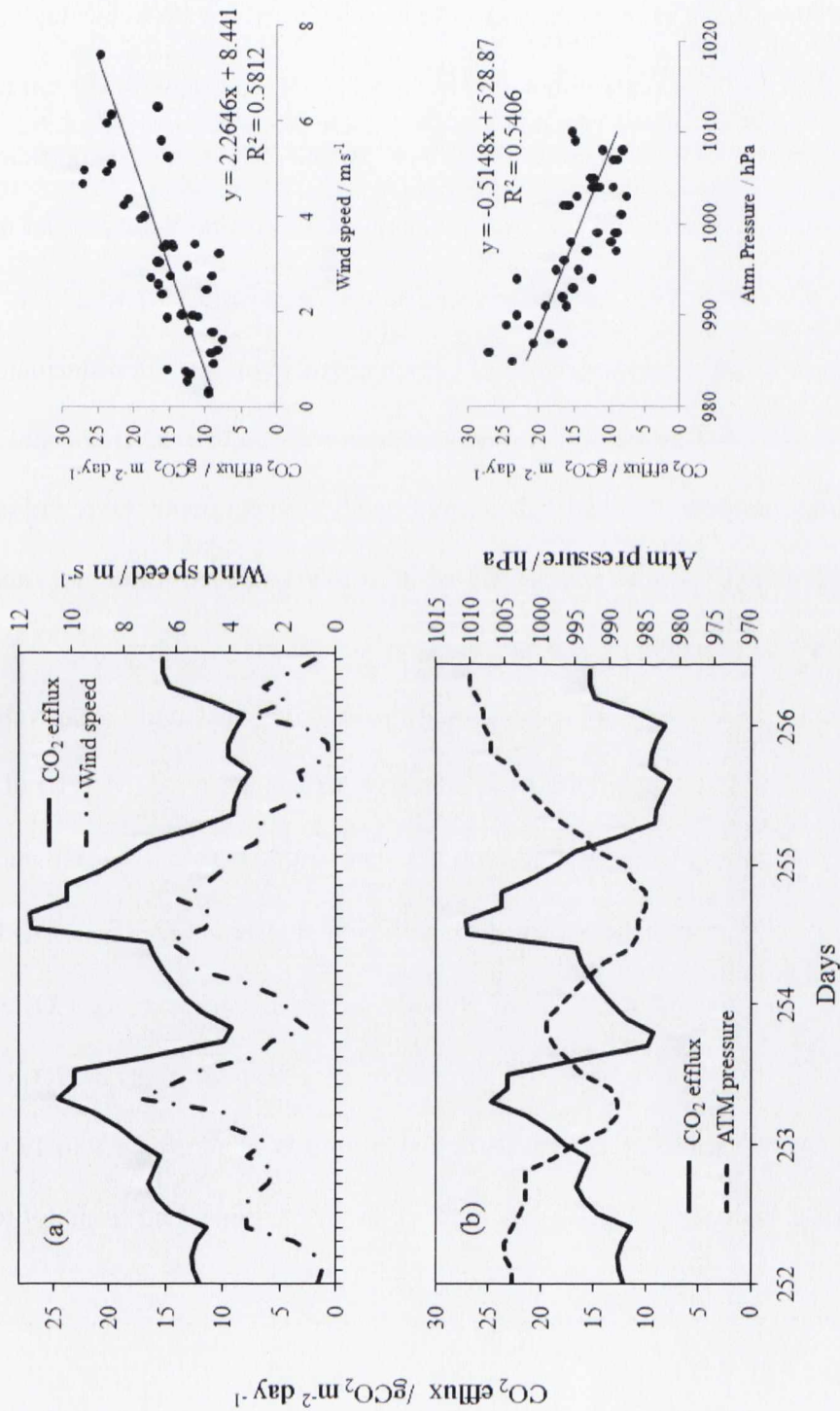


Figure 9: Influence of atmospheric pressure and wind speed on the soil CO₂ efflux. (a) Diurnal variation from DOY 253 to 257 (10th to 14th September 2008) of hourly mean values of CO₂ efflux and wind speed, and (b) CO₂ efflux with atmospheric pressure. On the right the respective correlations using the same data series.

3.3.5 Seasonal patterns of soil CO₂ diffusivity, concentration gradient and efflux

Figure 10 shows seasonal patterns based on hourly mean values between days of the year (DOY) 1 and 283 in 2008 of (a) soil moisture at 10 cm depth, and rainfall, (b) soil temperature at 10 cm depth, (c) soil CO₂ concentration gradient, (d) soil CO₂ diffusion coefficient, and (e) soil CO₂ concentration gradient efflux. At soil depth of 10 cm the hourly mean temperature varied between 6.1 and 16.5°C, and the soil moisture ranged from 15.7 to 27.1%. Analyzing the whole soil profile, hourly mean values of carbon dioxide concentration fluctuated between 423 and 2198 $\mu\text{mol mol}^{-1}$ at the soil surface, between 592 and 16212 $\mu\text{mol mol}^{-1}$ at 10 cm depth, and it varied between 844 and 42268 $\mu\text{mol mol}^{-1}$ at 20 cm depth. Over the same period at a depth of 40 cm the CO₂ concentration varied from 1439 to 26931 $\mu\text{mol mol}^{-1}$ and finally at 80 cm depth from 1013 to 33963 $\mu\text{mol mol}^{-1}$.

The quadratic function model approach (Eqn. [8]) fitted the half hourly mean values of CO₂ concentration gradient ($\Delta C/\Delta Z$) with a mean absolute percentage error (MAPE) of 24.3%. In particular, the mean hourly CO₂ concentration gradient ranged between 4×10^5 and 6.9×10^6 $\mu\text{mol m}^{-3} \text{ m}^{-1}$, and the mean value of soil CO₂ diffusion coefficient D_s (Eqn. [6]) had values ranging from 8×10^{-7} and $2.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. Finally, hourly mean estimated CO₂ efflux from the two sites had a difference of about 14.4%. The mean averaged values of CO₂ efflux from the two sites fluctuated from 1.1 to 6 $\text{gCO}_2 \text{ m}^2 \text{ day}^{-1}$ in the Winter, from 1.9 to 17.6 $\text{gCO}_2 \text{ m}^2 \text{ day}^{-1}$ in the Spring, from 4.9 to 27.1 $\text{gCO}_2 \text{ m}^2 \text{ day}^{-1}$ in the Summer, and from 4.9 to 23 $\text{gCO}_2 \text{ m}^2 \text{ day}^{-1}$ in the Autumn.

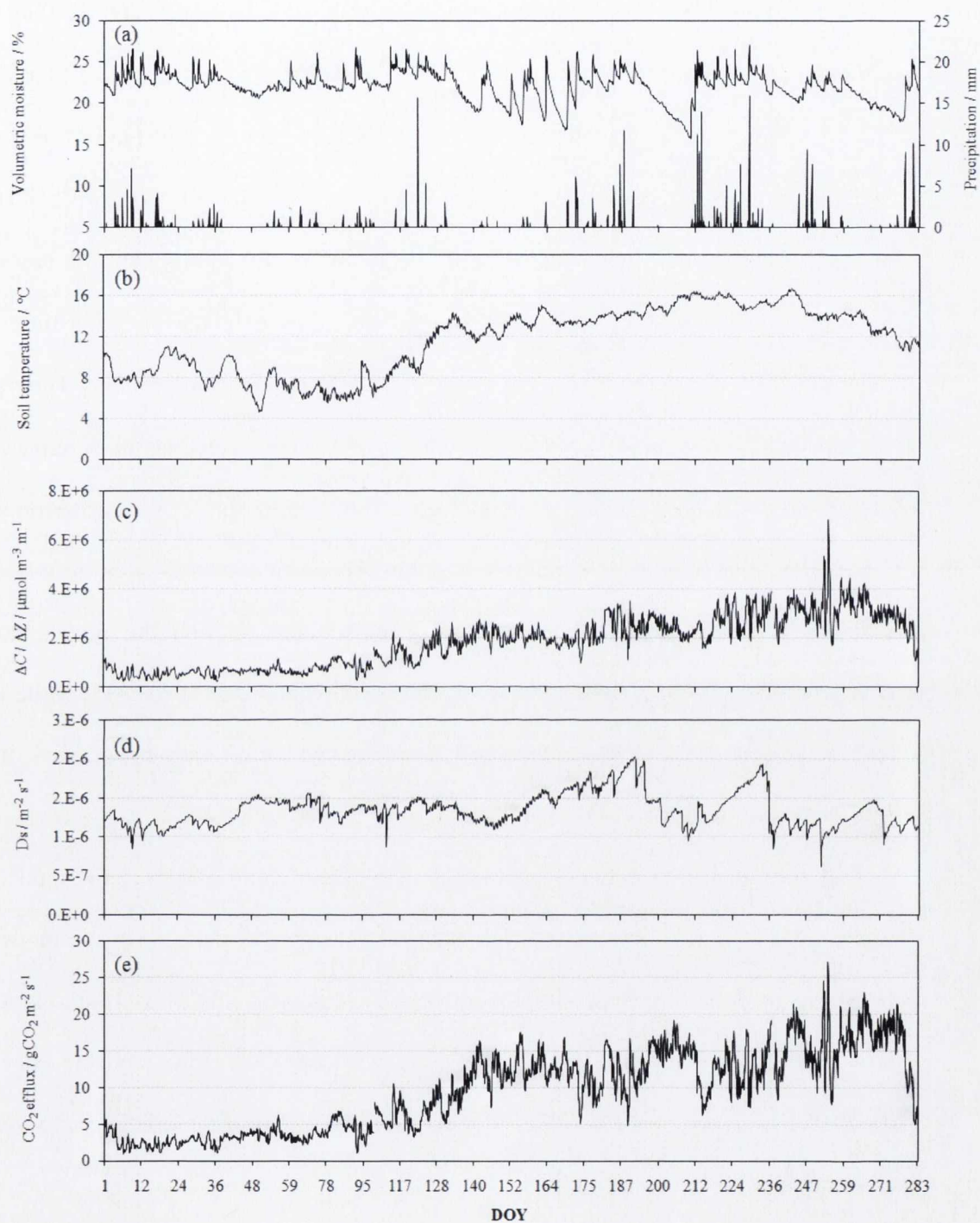


Figure 10: Time series from DOY 1 to 283 in 2008 of: (a) hourly mean precipitation and volumetric soil moisture at 10 cm depth, (b) soil temperature at 10 cm depth, (c) CO₂ concentration gradient, (d) soil CO₂ diffusion coefficient, and (e) estimated CO₂ efflux.

In order to better describe the seasonal relationships between the CO₂ flux and the climatic variables measured at the station, we used multiple regression analysis (MRA) to build a linear model in which the dependent variable was the natural logarithm of the CO₂ efflux ($\ln F_{CO_2}$), and the independent variables were soil temperature, and soil moisture at 10 cm depth, atmospheric pressure, wind speed, and precipitation. By using forward multi regression analysis, the independent variables were entered into the model one at a time in an order determined by the strength of their correlation with the criterion variable. The variables that did not add any significant success to the model were excluded. In summary, the MRA performed two models. Model A refers to the first stage in the forward criterion when all the independent variables were used as a predictor. Whereas, model B refers to the second stage when the atmospheric pressure was the variable excluded. For both the models the correlation coefficient between the predicted, and the observed values was $R = 0.843$; while the variance in F_{CO_2} accounted for by the independent variables, which measure the success of the model, was 71 % (adjusted $R^2 = 0.71$) (Table 2).

The atmospheric pressure, which had no significant contribution to the model ($p=0.357$), was excluded by the forward criterion, but without improving the R^2 of the model (Table 2). However, model B showed an improvement of the b coefficients which represent a measure of how strongly each independent variable influenced the CO₂ efflux, and the improvement of the t -test associated to the b values indicated a greater impact the predictors to assess the soil CO₂ efflux.

Model Summary ^(c)						
Model	R	R Square	Adjusted R Square		Std. Error of the Estimate	
A	0.843	0.710	0.710		2.99721	
B	0.843	0.710	0.710		2.99711	
Coefficients ^(c)						
Model	Predictors	Unstandardized Coefficients		Standardized Coefficients	t	Sig. (p)
		B	Std. Error	Beta		
A	(Constant)	22.185	6.345		3.497	0.000
	Prec.	0.198	0.064	0.036	3.071	0.002
	Atm. pressure	-0.006	0.006	-0.012	-0.922	0.357
	Soil temp.	1.251	0.021	0.714	60.768	0.000
	Soil moisture	-1.016	0.037	-0.337	-27.278	0.000
	Wind speed	0.250	0.048	0.062	5.172	0.000
B	(Constant)	16.391	0.868		18.882	0.000
	Prec.	0.206	0.064	0.037	3.213	0.001
	Soil temp	1.253	0.020	0.715	61.171	0.000
	Soil moisture	-1.006	0.036	-0.334	-28.058	0.000
	Wind speed	0.262	0.046	0.066	5.664	0.000

Table 2:Forward multiple regression analysis where each predictor was add into the models A and B one at a time in an order determined by the strength of their correlation with the dependent variable. The effect of adding each is assessed as it is entered, and variables that do not significantly add to the success of the model are excluded. The dependent variable (c) was: lnCO₂ efflux. The Standardized Beta Coefficients give a measure of the contribution of each variable to the model. A large value indicates that a unit change in this predictor variable has a large effect on the dependent variable. The t and Sig (p) values give a rough indication of the impact of each predictor variable – a big absolute t value and small p value suggests that a predictor variable is having a large impact on the criterion variable.

The regression line defined by the model:

$$\ln(F_{CO2})= 22.185 + (1.251 \times S.Temp) - (1.006 \times S.Moist.) + (0.262 \times Wind\ speed) + (0.206 \times Precipitation)$$

showed that the soil temperature had the largest impact on the soil CO₂ efflux (b=1.251), and as expected a positive relationship with soil respiration. While, soil moisture had the second largest impact (b=-1.006), but showing a negative relationship with F_{CO2}. Finally, the wind

speed and precipitation showed both a similar positive effect on the soil CO₂ flux, with a b coefficient of 0.262 and 0.206 respectively. In conclusion, the linear equation resulted from the MRA was verified by using the dataset of the year 2008 from DOY 1 to 283 with the (Figure 11).

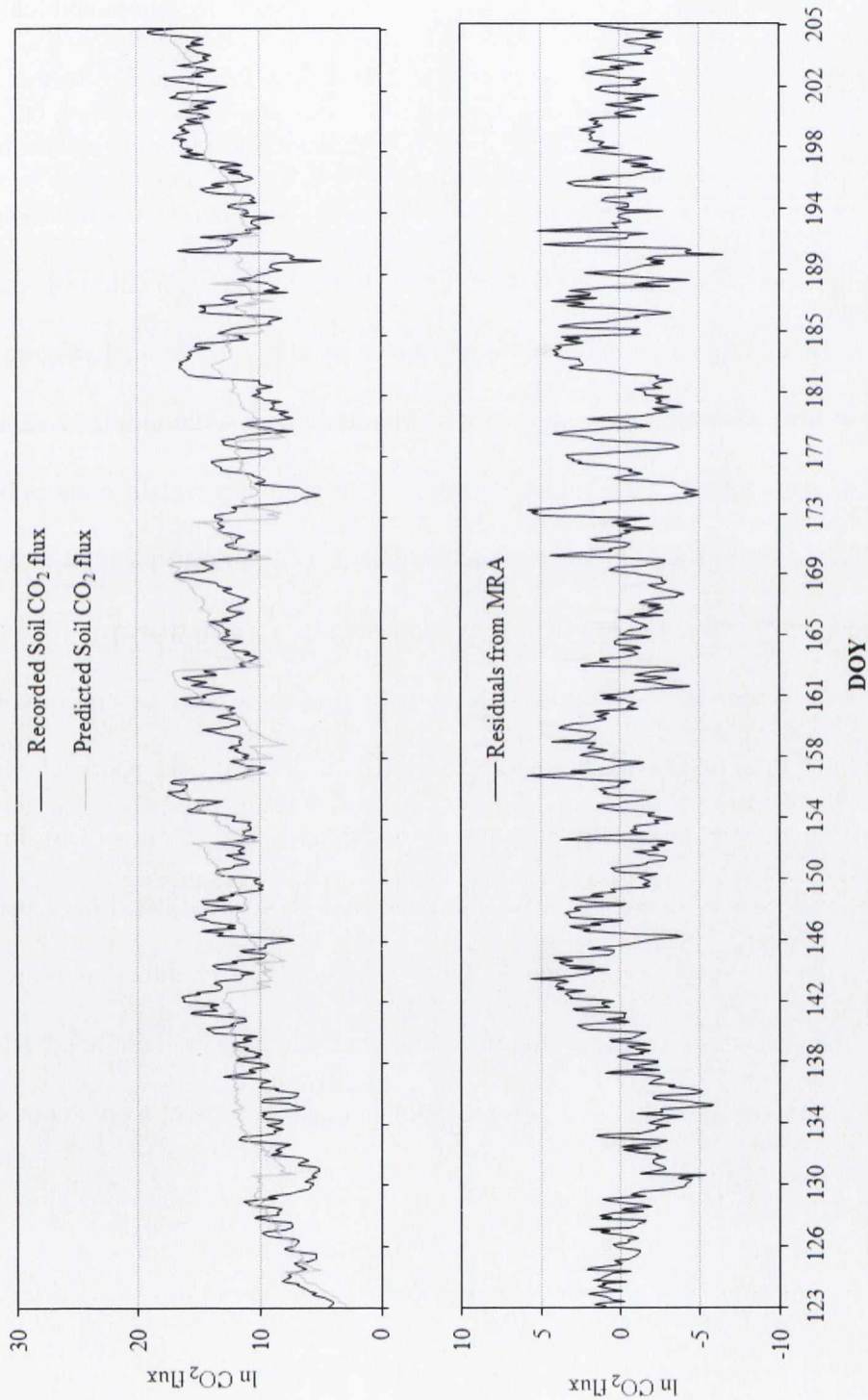
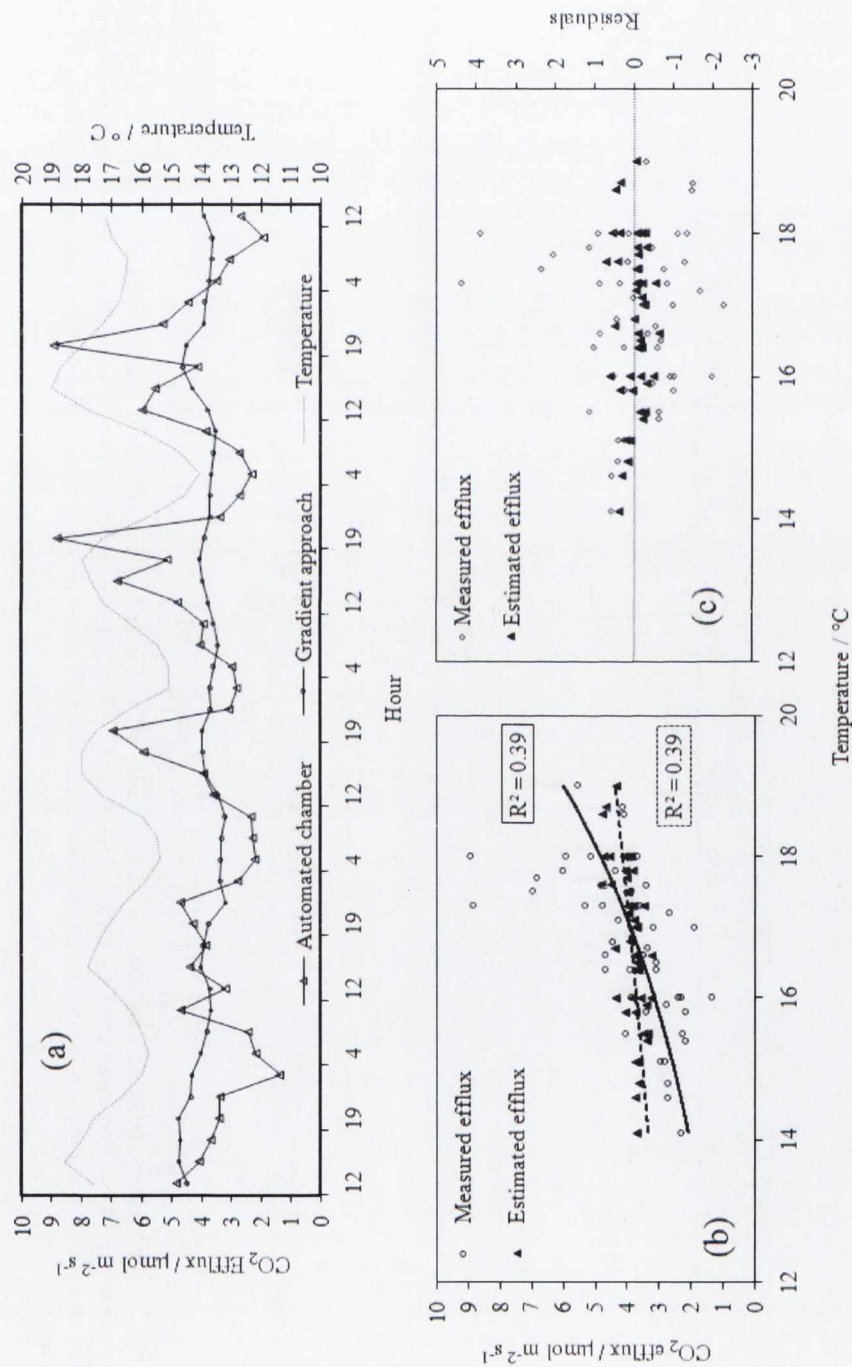


Figure 11: The quality of the MRA (gray line) is verified by using the dataset of soil CO₂ efflux (black line) expressed as $\ln \text{CO}_2$, from DOY 123 to 205 (from 3rd of May to 24th July). Also shown below the residual error terms of the MRA from the same data series.

3.3.6 Carbon dioxide efflux validation

Figure 12a and 13a show continuous measurements using the automated chamber, and estimated values, using the gradient approach, of CO₂ efflux from the 25th to the 30th of July and from 25th to 28th of September 2008. In July, both the carbon dioxide efflux measured by the automated chamber and the estimated CO₂ efflux showed identical correlation ($R^2=0.39$) with soil temperature at 10 cm depth (Figure 12b), although the examination of residuals gave a less biased distribution of residuals for the gradient approach valued (Figure 12c). The automated chamber measured the CO₂ efflux with greater diurnal amplitude of values than the estimated gradient approach efflux. Despite the large diurnal patterns differences between the two methods, during the study period reported in Figure 12 the mean value of soil CO₂ efflux estimated, and measured, ranged from 4.01 to 3.9 $\mu\text{mol m}^{-2} \text{s}^{-1}$ respectively.

In September in the presence of lower soil temperature values, the carbon dioxide effluxes measured by the automated chamber and estimated with the gradient approach (Figure 13a) showed a different exponential relationship with soil temperature (Figure 13 b). In particular, the estimated efflux had a better R^2 than the measured efflux (0.28 and 0.19 respectively). However, similar to the data collected in July, the automated chamber measured the CO₂ efflux with greater diurnal amplitude of values than the estimated gradient approach efflux. In addition, the mean values of soil CO₂ efflux, estimated and measured, were about 4.5 and 5.5 $\mu\text{mol m}^{-2} \text{s}^{-1}$ respectively.



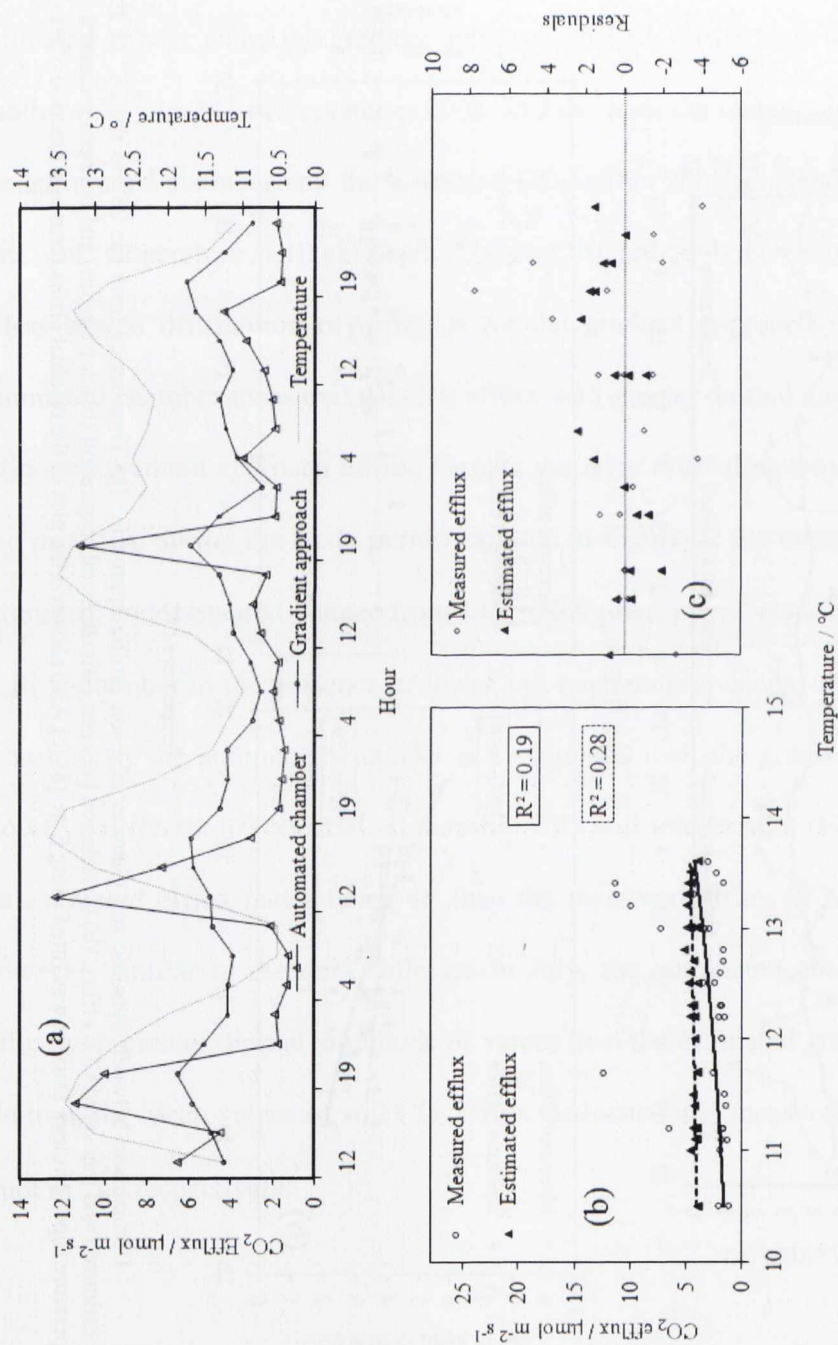


Figure 13: Comparison between dynamic soil chamber and soil profile approach. (a) Time series from the 25th to the 28th of September of soil temperature, estimated and measured CO_2 efflux. (b) Correlation between estimated soil respiration (black triangles) and between measured respiration and soil temperature (open circles). Dataset was fitted using. [8] (c) Also shown is the plot of the residual errors term as a function of temperature.

3.3.7 Soil profile temperature sensitivity of soil respiration

The exponential function (Eqn. [5]) fitted to the mean daily values of gradient-based soil respiration indicated that CO₂ efflux was mainly driven by temperature, although other confounding factors like soil moisture, atmospheric pressure, and wind speed, affected such correlation. Examining the variability of the temperature sensitivity along the soil profile, from soil surface to 80 cm depth the Q_{10} values ranged from 4.3 to 7.6 respectively (Figure 14). An increase of apparent Q_{10} with depth was seen in all studies, and it is typically explained as a result of a correlation between the CO₂ effluxes produced at a certain soil depth with a temperature measured at a different soil depth. However, the lower R^2 between soil CO₂ efflux and temperature at the soil surface may be indicative of near soil surface-atmosphere induced processes which affected the seasonal fluctuation of the temperature at soil surface. Considering that the soil profile layer between 0 and 10 cm contributed approximately from 0 to 81% of the total CO₂ produced within the 80 cm profile study (Chapter 5), a Q_{10} values ranging from 4.3 to 6.1 appeared to be the more realistic value in our site.

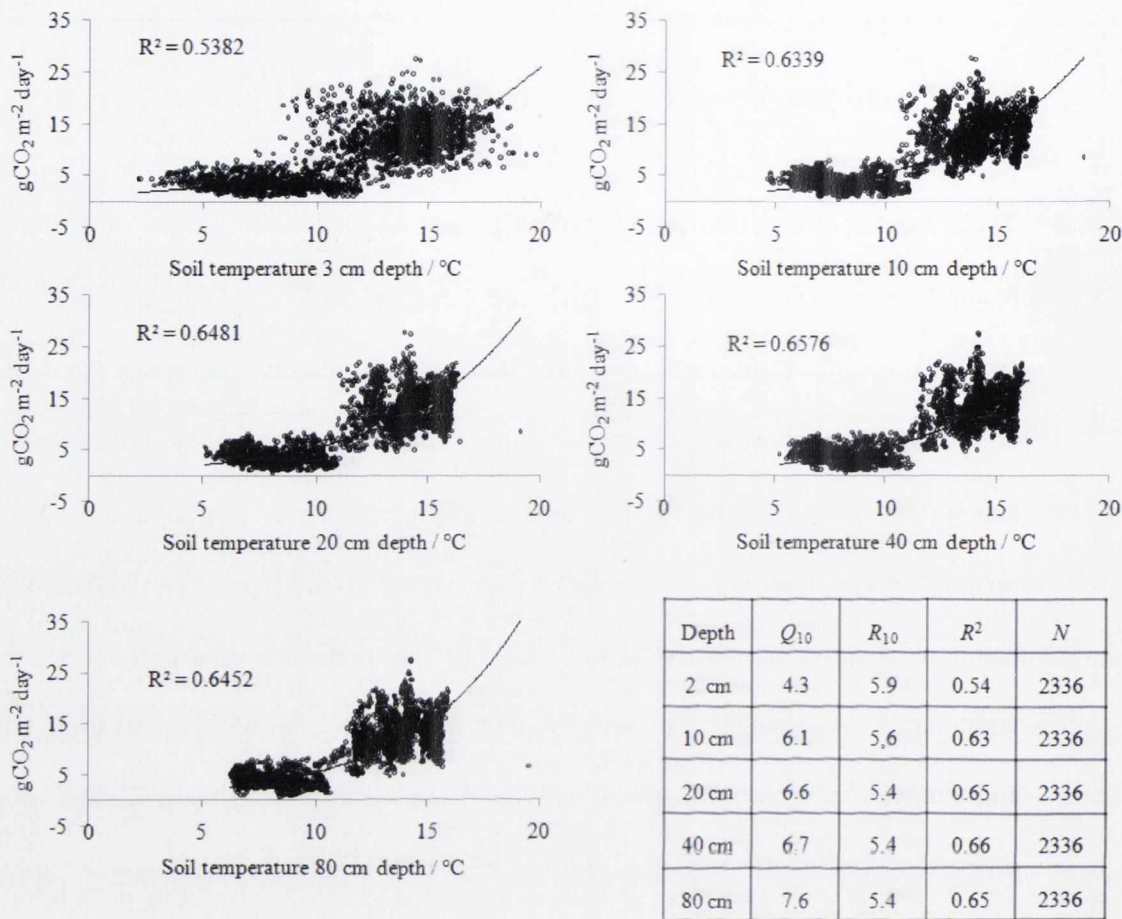


Figure 14: Relationship between estimated soil CO₂ efflux and soil temperature at 3, 10, 20, 40, and 80 cm depth. Data were fitted using Eqn. [5]. On the right also shown the respective temperature sensitivity values (Q_{10}), the value of temperature at 10 °C (R_{10}), the correlation fit (R^2), and the number of values used (N).

3.4 Discussion

The importance of obtaining better estimates of ecosystem CO₂ soil efflux, and to understand the factors controlling its temporal variability, has raised interest in soil profile CO₂ efflux studies. It is widely accepted that environmental parameters can affect the rates of soil CO₂ respiration not only temporally at daily and seasonal scale, but also spatially at a vertical and horizontal dimension. The use of manual and automated soil surface chamber has resulted an

efficient method to measure CO₂ efflux at soil surface, and to capture its spatial variability from almost any type of landscape. However, only with the employment of soil profile approach techniques it has been possible to have information on vertical distribution of respiration activity.

Calculation of CO₂ efflux using Fick's Law (Eq. [1]) can be challenging. The ability to calculate CO₂ efflux depends on both an accurate estimation of vertical CO₂ concentration gradient ($\Delta C/\Delta Z$) and soil CO₂ diffusion coefficient (D_s). Their variability is linked to the interacting effects of environmental factors such as: (a) the increased production of CO₂ in the soil, due to more favorable soil temperature (b) the changes in soil CO₂ diffusivity due to increase and decrease of air-filled pore space, (c) the degassing effect which occurs at the initial stages of the rainfall event, which contribute to the decrease of diffusivity and therefore to the increase of CO₂ concentrations at all soil depths, and (d) to wind-induced pressure pumping (Davidson and Trumbore, 1996; Fang and Moncrieff, 1999; Irvine and Law, 2002; Jassal et al., 2005; Borken et al., 2003; Yuste et al., 2004; Tackle et al., 2004; Lee et al., 2002). Drewitt et al. (2005) found that the vertical profile of soil CO₂ concentration had similar shapes throughout the year and between consecutive years of their experiment. We found that the CO₂ concentration along the five measuring points of the soil profile had a characteristic quadratic shape skewed towards the bottom of the profile, and with maximum CO₂ concentration values generally at 40 cm depth. The quadratic function model (Eq. [8]) fitted well the measured CO₂ concentrations, and also described well the natural behavior of $\Delta C/\Delta Z$ during most of the soil and atmospheric conditions. Throughout the measurements of 2008 the discrepancy between the measured values of vertical CO₂ concentration and the values

estimated by the quadratic function model was about 24.3% as mean absolute percentage error (MAPE). As expected, we found that $\Delta C/\Delta Z$ followed diurnally, weekly and seasonally soil temperature patterns, and rapid changes of volumetric water content due to rainfall events, atmospheric pressure, and wind speed reduced its relationship with the soil temperature (Figure 15).

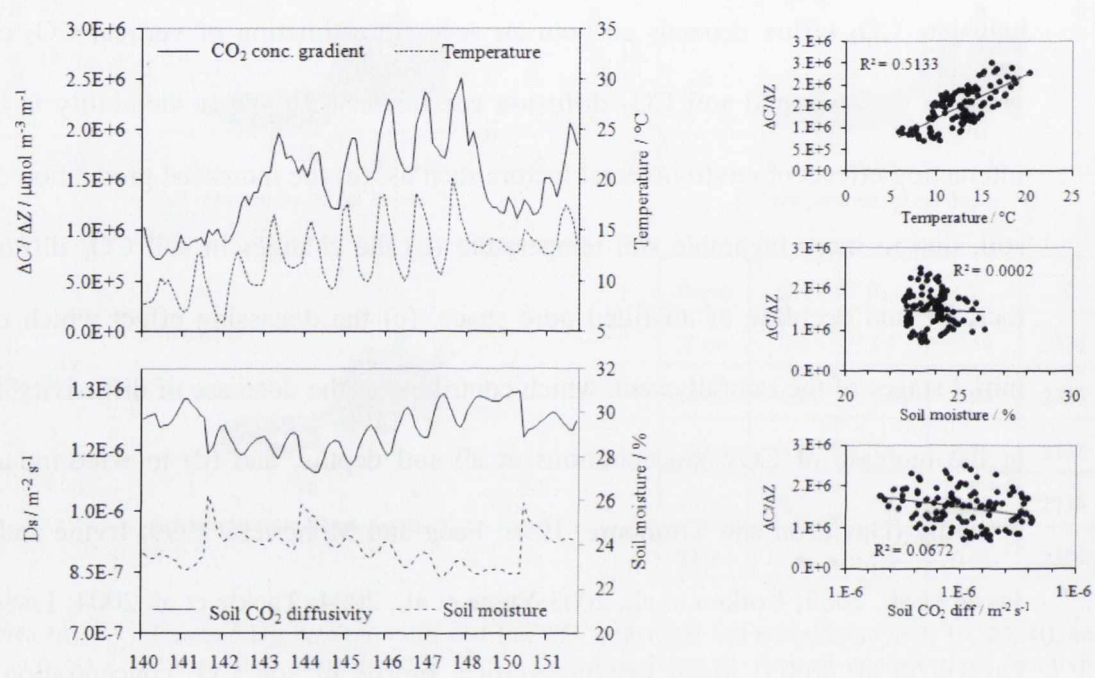


Figure 15: Influence of soil temperature, soil moisture, and soil CO₂ diffusivity on CO₂ concentration gradient. Weekly variation from DOY 140 to 151 (20th to 31st May 2008) of: (a) hourly mean values of CO₂ concentration gradient and soil temperature at 10 cm depth, (b) soil CO₂ diffusivity and soil moisture at 10 cm depth. Also shown on the right the correlation between soil CO₂ concentration gradient with soil temperature soil moisture, and soil CO₂ diffusivity.

Earlier experiments attributed the lack of coincidence between the diurnal phase of CO₂ concentration and temperature at the soil surface as an effect of air turbulence (Hirsch et al., 2002; Jassal et al., 2005). Indeed, the simultaneous influence of environmental factors such as rainfall, atmospheric pressure, and wind speed affect the CO₂ movement at the boundary layer between soil and atmosphere, affecting also $\Delta C/\Delta Z$ and the relationship of the CO₂ efflux with

the soil temperature.

Extensive research has been done in the past to obtain an accurate estimate of D_s either from the use of models or by direct measurements. From a retrospective analysis of the literature, the use of popular models such as Penman (1940), Marshall (1959), Millington-Quirk (1961), Moldrup et al. (1999), and measurement techniques like those reported by Liang et al. (2004), Jassal et al. (2005), and DeSutter et al. (2008) appeared not to provide a universally acceptable method to estimate D_s . Tang et al. (2003) reported that in rocky silt loam soil CO_2 efflux estimated using the Millington-Quirk and Marshall models were overestimated by 9 and 18%, respectively. DeSutter et al. (2008) showed that measured soil-specific D_s values determined for Harps loam soil were 2.5 times lower than those predicted using Moldrup and Millington-Quirk models. In contrast, Jassal et al. (2005) reported an underestimation of the Millington-Quirk model comparison to measured soil-specific D_s values in sandy soil. By running the Millington-Quirk model, we found that in our soil profile D_s (Eq. [2, 4]) ranged from 8×10^{-7} to $2.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. As expected, D_s was strongly dependent by soil moisture and its values sharply decline after rainfall events due to the decrease of the air-filled soil porosity (Figure 10 and 15).

Irrespective of the method used to predict $\Delta C/\Delta Z$, and D_s , estimates of carbon dioxide efflux using the gradient approach have to be compared with CO_2 efflux measured at soil surface by chambers. This is essential not only to evaluate the results of the estimated efflux, but also to integrate them with the results of the chamber measurements. Many researchers have attempted the comparison of soil profile CO_2 efflux with soil surface chambers. Tag et al. (2003), reported that the efflux calculated from the concentration gradient was 9%

underestimated compared to measured efflux. They also suggested that the difference between the two methods was due to the soil diffusivity calculation. Liang et al. (2004) showed even higher discrepancies between estimated and measured CO₂ effluxes, and reported an overestimation of approximately 45%. Jassal et al. (2005) using solid-state sensors, showed a close agreement between the two methods, highlighting a tendency of overestimating at low and medium effluxes and underestimation for high effluxes. Overall, our results indicated that continuous measurements of soil surface CO₂ efflux agreed well in terms of mean daily values with soil profile CO₂ efflux. Depending on the environmental condition (Figure 12, and 13) the two methods provided similar mean values of soil CO₂ efflux, 15.2 and 14.8 gCO₂ m² day⁻¹ in July, 17.1 and 20.9 gCO₂ m² day⁻¹ in September respectively for the measured and estimated CO₂ efflux. A point of interest in these results is the measurement of CO₂ concentration at soil surface, which permitted a better estimation of the soil concentration gradient at the boundary layer between soil and atmosphere, and therefore to better estimate the CO₂ efflux. The use of a diffusion chamber designed for measuring CO₂ concentration at soil surface, without altering its natural behavior, allowed us to accurately measure the CO₂ concentrations at soil surface, even in presence of air turbulence, and rainfall events. However, the gradient-based CO₂ effluxes showed lower diurnal fluctuation than the measured efflux. This difference could be due to a combination of factors such as the use of a linear regression to estimate D_s throughout the soil profile (Eqn [4]), as well as biases in chamber-based measurements related to pressure differences, induced by the wind, inside and outside the chamber (Davidson et al., 2002; Suleau et al., 2009). The calculation of D_s based on harmonic averaging of individual diffusivities of each profile layer, which resembles the slope of the

linear regression between the individual D_s of each layer and the depth, would not always represent the natural condition of D_s throughout the soil profile. Within the soil profile the effect of temperature, water content, and wind speed on D_s is relative to the depth as well as the horizon characteristic. Therefore, as for the $\Delta C/\Delta Z$, the development a site-specific CO_2 diffusion model value would further improve the estimation of the CO_2 efflux at soil surface.

At a daily scale soil temperature appeared to be the primary environmental driver of the soil CO_2 efflux rates (Figure 5). During the growing season the apparent differential response of soil CO_2 efflux to soil warming and cooling led to a diurnal hysteresis behaviour of the soil respiration. This could be related to changes in the pool of labile substrate availability for the heterotrophic component, which counteract the effect of temperature, and thereby the temperature dependence of soil respiration (Gut at al., 2004; Kirshbaum, 2006), as well as to changes in plant phenology and photosynthesis. Generally the hysteresis in soil respiration are attributed to the production and translocation of photosynthate from the leaves, through the phoelem and to the roots and associated microbes. However, Riveros-Iregui et al. (2007) reported that such hysteric, non linear behaviour in soil CO_2 efflux and soil temperature may limit the ability of many power or exponential models to adequately predict soil respiration as a function of soil temperature. We found that the hysteresis effect reduced the daily correlation between the CO_2 efflux and the soil temperature. Moreover, we also found a phase shift between the daily peaks of CO_2 efflux and soil temperature which increased during the growing season reaching a maximum time lag of approximately three hours (Figure 6, 7).

Generally the correlation of soil respiration with soil temperature is affected by the counteracting effect of soil moisture fluctuations due to rainfall events, atmospheric pressure,

and wind speed (Millington, 1959; McCarty et al., 1999; Renault et al., 1998; Massman et al., 1997; Fang and Moncrieff, 1999). We found that above all, on a weekly basis, the rapid fluctuation of soil water content negatively affected the correlation of soil CO₂ efflux to soil temperature (Figure 8). Moreover, during highly unsettled weather conditions, wind speed and atmospheric pressure played a fundamental role in controlling the soil CO₂ emissions (Figure 9). Several field studies with multiple temperature measurements with depth (Xu and Qi, 2001; Hirano et al., 2003; Tang et al., 2003; Gaumont-Guay et al., 2006; Khomik et al., 2006; Shi et al., 2006; Wang et al., 2006; Pavelka et al., 2007) showed an increase of apparent Q_{10} with depth. Graf et al. (2008), using a comprehensive data set of observed variability of the Q_{10} dependence on temperature measurement depths, showed that when patterns of soil CO₂ efflux are correlated to temperature patterns with smaller amplitudes, and higher phase shift, can result in an underestimation of Q_{10} in field experiments. Our results showed that the variability of the temperature sensitivity along the soil profile, from soil surface to 80 cm depth, ranged from 4.3 to 7.6 respectively. Contrary to other studies (Paul et al., 1999) that reported better correlations of CO₂ efflux with air temperature than with soil temperature, in our site the R^2 values improved when soil profile temperature between 10 and 40 cm depth were considered. The lower correlation value at soil surface could be explained by the effect of near soil surface-atmosphere induced processes which affect the seasonal fluctuation of the temperature at soil surface, while, the better correlation of our CO₂ efflux rates with deeper soil temperature is due to a coincidence between the depth of measured temperature and soil CO₂ production (Chapter 4).

3.5 Conclusion

Here we explored, and validated, the use of high-temporal resolution soil CO₂ concentration profile to assess soil CO₂ effluxes using a diffusivity and gradient-based model. Overall, the experiment highlighted the influence of environmental parameters such as soil temperature, water content, atmospheric pressure and wind speed on soil profile CO₂ efflux. Gradient soil CO₂ efflux was well correlated diurnally, weekly, and seasonally to soil temperature. As found in previous temperature sensitivity studies, we observed an apparent increase of Q_{10} with increasing depth of soil temperature used.

During the growing season, we found an increasing hysteresis effect of soil respiration due to a differential response of soil CO₂ efflux to soil warming and cooling, which decreased the correlation between the soil respiration and the soil temperature, and increased the phase shift between the daily peaks of CO₂ efflux and soil temperature. These results would certainly profit from the application of continuous carbon stable isotope studies, and from manipulation experiments, such as girdling or controlling temperature. The linkage between photosynthesis and soil activity is still not entirely explained, and the use of technique such as soil diffusion chamber, which permit continuous and precise measurements of soil CO₂ concentration, combined with the use of partitioning methods to estimate the contribution of individual sources to total soil CO₂ efflux would clearly be an advantage.

The modeled soil CO₂ efflux profile showed good agreements with measurements of surface chamber efflux. however the study highlighted the importance of reliable estimation of the vertical soil CO₂ diffusion coefficient. Although several models, and soil-specific measuring methods, have been developed to determine D_s at generic soil depths, further

research is needed to develop profile-specific diffusion models able to better estimate D_s changes throughout the soil profile.

Chapter 4

Vertical partition of CO₂ production rates in the soil profile. A case study using high-temporal resolution CO₂ concentrations

Summary

Large uncertainties remain regarding the response of soil subsurface respiration processes to climate change. The impact of global warming on soil CO₂ emissions could differ with soil depth and depend on local conditions could vary among different ecosystems. The partitioning of soil CO₂ effluxes within the soil profile is a powerful tool for the assessment of season patterns of subsurface CO₂ production and its dependence to environmental drivers such as temperature and water content. The objectives of this study were to evaluate how the relative contributions of CO₂ production by soil profile layers in a *Miscanthus* × *giganteus* stand varied seasonally and in relation to soil temperature and water content. High temporal resolution CO₂ concentrations profile, soil temperature, water content, and soil physical characteristics measurements were used to model the effective soil CO₂ diffusivity, and to assess the CO₂ flux at the top of each soil layer and the CO₂ production within each layer.

Soil CO₂ production rates showed that over four seasons the top layer (0-10 cm) contributed on average 59% of total soil CO₂ efflux, the 10-20 cm layer 35%, the 20-40 cm layer 6%, and the bottom layer (40-80 cm) had a negligible contribution. Surface flux more closely followed changes of CO₂ production in the top 20 cm of the soil profile. Moreover, the temperature sensitivity of CO₂ production varied down the soil profile, as well as the relationship with the soil water content.

4.1 Introduction

It is widely agreed that more studies are required to enhance our understanding on the role of soil processes in controlling soil respiration. It is important to evaluate soil respiration at several depths and investigate the response of deep-soil respiration to different environmental conditions. The impact of global warming on soil respiration is strongly related to the characteristics of deep-soil carbon. Trumbore (1993), using radiocarbon measurements, compared the carbon dynamics in tropical and temperate soils and showed that the majority of the organic carbon in the upper 22 cm of tropical soil had a residence time of 10 years or less; while, residence time of soil organic carbon in temperate forest was found to vary from 10 to 1,000 years.

To date several studies through field observations have highlighted the importance of the processes related to CO₂ diffusivity and transport of soil CO₂ (De Jong and Schappert, 1972, Campbell and Frascarelli, 1981, Osozawa and Hasegawa, 1995, Freijer and Leffelaar 1996, Davidson and Trumbore, 1995, Irvine and Law, 2002, Lee et al., 2002, Hirsch et al., 2002, Borken et al., 2003, Tang et al., 2003, Yuste et al., 2004, Tackle et al., 2004, Drewitt et al.,

2005, Jassal et al., 2005, DeSutter et al., 2008). Generally, CO₂ concentration in the soil air space between soil particles is an order of magnitude higher than in the atmosphere (Fernandez and Kosian, 1987; Šimunek and Suarez, 1993) resulting in a large concentration gradient from deep layers to the atmosphere. Two major processes control the CO₂ emission from soil: (i) the production of CO₂ in the soil and (ii) its transport from the soil to the atmosphere. The movement of the CO₂ in the soil occurs through a continuous network of air-filled pore spaces that connect the deeper layers to the surface of the soil, and gaseous diffusion and advective flow are considered to be the most important mechanisms of CO₂ movement throughout soil profile, with the contribution of liquid phase diffusion being significant only in soil close to saturation (Šimunek and Suarez, 1993).

Few studies have investigated the relative contribution from different depth layers to total CO₂ production from the soil. Davidson and Trumbore (1995) measured the production of CO₂ in deep soils of the eastern Amazon and found that about 70–80% of CO₂ production in forest and pasture in the Amazon basin occur within the top 1 m of soil. Gaudinski et al. (2000) calculating the CO₂ flux at each depth, using Fick's first law and a radiocarbon inventory, found that 63% of soil respiration took place in the top 15 cm of the soil in a temperate forest. Jassal et al. (2005) under a 54-years old Douglas forest on Vancouver Island calculated that more than 75% of the CO₂ originated in the top 20 cm of soil. In a further study Davidson et al. (2006) estimated that in a mixed hardwood stand in Massachusetts the contribution of the *O* horizon was 40–48% of the total annual soil CO₂ efflux.

The relationships between deep soil CO₂ production, temperature, and soil water content have also been reported. Hirsch et al. (2002) investigated deep-soil respiration in a boreal forest and

found that at a depth of 50 cm it varied linearly with temperature. Risk et al. (2002) showed that, across four study sites of contrasting vegetation cover and land use, subsurface CO₂ production was mainly controlled by temperature. Davison et al., (2006) reported that both soil temperature and water content were significantly correlated with soil CO₂ efflux and CO₂ production rates from top soil profile. However, the contribution of the deep organic horizons to soil CO₂ efflux remain still unclear, as well as the effect of climate change on deep soil processes. Here we report the results of an investigation into the CO₂ profile production in a *Miscanthus × giganteus* stand in central of Ireland. Our objectives were (1) to assess soil production rates using continuous high temporal resolution measurements of CO₂ concentration profile, (2) to evaluate the relative contribution of CO₂ production from different soil profile layers, (3) to examine the seasonality of soil production rates, and (4) to explore the dependency of CO₂ production rates on soil temperature, water content and other environmental parameters throughout the soil profile. Considering the mean annual C of aboveground biomass residues falling to the ground (2.9 gC m⁻² day⁻¹), depending on the climatic conditions the top layer of the soil profile represented a significant transient source or sink of carbon on a seasonal basis.

4.2 Material and methods

4.2.1 Site description and soil characteristics

Measurements were carried out throughout 2008 in a 14 year old *Miscanthus x giganteus* stand

located at the Teagasc (Irish Agricultural Research Institute), Crops Research Centre, Oak Park, Carlow (52° 51' N, 6° 54' W, 50 m above sea level). The climate is Oceanic with no extremes of temperature. The mean annual air temperature at the site in 2008 was about 9.7 °C with summer mean daily maximum of about 19 °C and winter mean daily minimum is about 2.5 °C. The annual number of days with more than 1 mm of rain was about 180, and the average annual rainfall was about 1000 mm.

As described in Chapter 3.3.1, the soil of the *Miscanthus x giganteus* stand was classified, following the classification scheme for England and Wales (Avery, 1980), as a brown podzolic soil. Analysis of total soil organic carbon (TOC) and total nitrogen (N) were performed by elemental analysis (LECO), whereas the soil particle density (PD_s) was measured by submersion method (ASTM, 1992a). Finally, total bulk density (D_b) for each soil profile depth was determined using intact soil cores extracted manually from the soil profile. By drying each soil core in oven at 60 degrees for up to 7 days, and storing at room temperature for 2–4 weeks to redistribute the soil water content, each core was weighed, and successively tightly wrapped in polyethylene sheet to determine the volume by water displacement method.

4.2.2 Field measurements

Carbon dioxide concentration in the soil profile was monitored using the soil diffusion chamber technique (see Chapter 2). In essence, one surface diffusion chamber and four soil diffusion chambers were placed at depths of 0, 10, 20, 40 and 80 cm in the soil. Both the

surface and the soil diffusion chambers were connected by a pair of nylon sampling tubes, with inner and outer diameter of 0.4 and 0.6 cm respectively, to a multi-port valve system (ACL s.r.l, 20040 Cavenago di Brianza, Milan, ITALY), which feeds the gas sample into an infra red gas analyzer (Environmental gas monitor WMA-2; PP Systems Hitchin, Hertfordshire UK) with a flow rate of 50 ml min⁻¹. The output signals of the gas analyzers were collected every second, integrated over a period of 5 minutes, and stored on a datalogger (21-X, Campbell Scientific Inc.). The multi-port solenoid system performed a daily routine of nine sub-cycles measurements. Each sub-cycle measurement of 150 minutes allowed the sequential measurement of all five chamber depths for a duration of 30 minutes. For further technical details of this technique see Albanito et al. (2009).

Alongside the chambers at depths of 0, 10, 20, 40, 80 cm, soil volumetric water content and soil temperature were measured continuously using dielectric sensors (ECH2O EC-5 Decagon Devices, Inc., 950 NE Nelson Court, Pullman, WA, USA) and custom-manufactured Cu-Constantan thermocouples. Hourly measurements of precipitation were obtained using a tipping bucket rain gauge (Model ARG100, Campbell Scientific Ltd, Leicestershire, UK) and horizontal wind speed and direction was measured using a vane anemometer (Model 05103, R.M. Young Co., Traverse City, MI, USA) positioned 2 mt above the soil surface.

Output signals from the soil moisture probes, thermocouples, rain gauge, and anemometer, were recorded every minute and were integrated on an hourly basis and stored on a datalogger (CR-10x and CR-10, Campbell Scientific Inc.).

Finally, soil CO₂ efflux was also measured using an automated efflux chamber (ACE System, ADC BioScientific Ltd, UK). The soil collar of the automated chamber of 5 cm height

and 23 cm diameter was inserted into the soil a depth of 3 cm in close proximity to the soil profile CO₂ gradient system. Soil CO₂ flux was measured every 30 minutes and integrated to 150 minute averaged values.

4.2.3 CO₂ production in soil

To assess the soil carbon dioxide production throughout the soil profile, we partitioned the profile in four layers (0–0.1 m, 0.1–0.2 m, 0.2–0.4 m, and 0.4–0.8 m). CO₂ effluxes in each layer were calculated using Fick's first law:

$$F_{CO_2} = -D_s \Delta C / \Delta Z \quad [1]$$

Where F_{CO_2} is the flux of CO₂ ($\mu\text{mol m}^{-2} \text{s}^{-1}$), D_s is the soil diffusion coefficient of CO₂ in the soil ($\text{m}^2 \text{s}^{-1}$), C is the concentration of CO₂ ($\mu\text{mol m}^{-3}$), and Z is the depth below the soil surface (m). $\Delta C / \Delta Z$ is the gradient of CO₂ concentration at each depth, and it was obtained from the observed data of CO₂ concentration ($\mu\text{mol mol}^{-1}$). The soil CO₂ diffusion coefficient (D_s) was estimated using the Millington and Quirk model (Millington and Quirk, 1961):

$$\frac{D_s}{D_a} = \xi \quad [2]$$

where D_a is the CO₂ diffusion coefficient in the free air, $\xi = \frac{\varepsilon^{10}}{\phi^2}$ is the gas tortuosity factor (Jury et al., 1991), ε is the soil air-filled porosity, and ϕ is the total porosity of each layer ($\text{m}^3 \text{m}^{-3}$) calculated by the following equation:

$$\phi = \left(1 - \frac{D_p}{p D_s}\right) \times 100 \quad [3]$$

D_b (g cm^{-3}) is the bulk density, and PD_s (g ml^{-1}) is the particle density of the soil within each soil layer. As described in Chapter 3, D_b for each soil depth was determined using intact soil cores extracted manually from the soil profile. By drying each soil core in oven at 60 degrees for up to 7 days, and storing at room temperature for 2–4 weeks to redistribute the soil water content, each core was weighted, and successively tightly wrapped in polyethylene sheet to determine the volume by water displacement method.

Assuming that the CO_2 concentrations throughout the soil profile remained close to a steady state condition over time, the gradient of CO_2 efflux between adjacent layers indicated the CO_2 production rate from each layer. In other words, the production at each depth was calculated from the difference between the outward output flux from layer i minus input flux from layer $i - 1$ below:

$$\alpha_i = F_i - F_{i+1} \quad [4]$$

Combining [1] and [4] we obtain:

$$\alpha_i = \left[De_i \left(\frac{c_i - c_{i-1}}{z} \right) \right] - \left[De_{i+1} \left(\frac{c_{i+1} - c_i}{z} \right) \right] \quad [5]$$

where De_i is the effective diffusivity for the layer i . This was extended from the soil surface to maximum sampling depth (Davidson and Trumbore, 1995).

Figure 1 shows this calculation in diagrammatic form. α_i represents the CO_2 production at the profile. To calculate the fluxes at layer 0–0.1, 0.1–0.2, 0.2–0.4, and 0.4–0.8 m, soil temperature, water content, and soil CO_2 diffusivity at each measuring point and time in the soil layers were averaged.

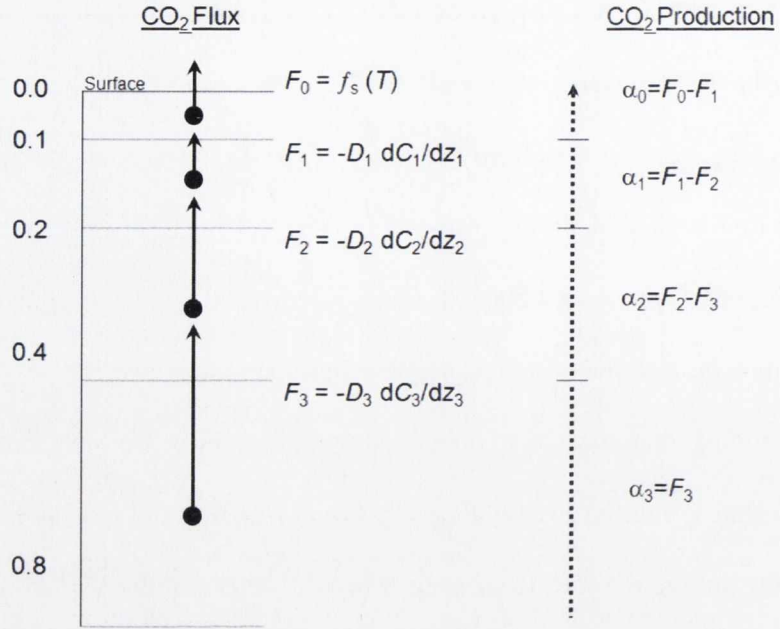


Figure 1: Diagram of the partitioning model used to evaluate the CO₂ production rate at each depth in the Carlow site. F_i is the soil CO₂ flux, D_i is the gas diffusion coefficient, dC_i/dz_i is the gradient of the soil CO₂ concentration, and α_i is the CO₂ production rate. Note that although a gas flux is represented by an arrow pointing upward, a downward flux is also possible, potentially at the bottom of the soil profile.

4.2.4 Data analysis

The seasonal temperature sensitivity of soil CO₂ production rates was assessed fitting the daily mean CO₂ production values with the van 't Hoff expression:

$$\alpha = \alpha_{10} \cdot Q_{10}^{\left(\frac{T-10}{10}\right)} \quad [6]$$

where α is the soil CO₂ production rate, α_{10} is the simulated soil production at a temperature of 10 °C, Q_{10} is the change in CO₂ production resulting from a 10°C increase in temperature, and T is the daily mean values of soil temperature measured at 10 cm depth

4.3 Results

4.3.1 Site and soil profile characteristics

At the end of the growing season (October 2007) the standing biomass (B_0) of *Miscanthus × giganteus* was about 15.4 t ha⁻¹, whereas in early spring 2008 the standing dry biomass remaining (B_1) before the final harvest was about 13.1 t ha⁻¹ (data collected by the ecophysiology group of Botany department). By summing the quantity of pre-harvest losses at the site ($B_0 - B_1$), the stubble biomass remaining to the soil after the final harvesting, and the total RDW (including rhizomes), the 2007-2008 rate of total annual biomass residues falling and remaining to the ground was estimated to be 6.74 g DM m⁻² day⁻¹, which considering an average value of 43% C for the *Miscanthus* plant residues it corresponded to about 2.85 g C m⁻² day⁻¹. The vertical distribution of the *Miscanthus × giganteus* rooting system was confined within 60 cm of soil depth, of which 82% was found in the top 30 cm. Total soil organic carbon (TOC) varied from 43.1 g kg⁻¹ to 10.1 g kg⁻¹ at 80 cm depth, while the total nitrogen (N) varied from 36 g kg⁻¹ to 7.3 g kg⁻¹. Finally, total bulk density (D_b) varied from 1.07 g cm⁻³ to 1.54 g cm⁻³ (Table 1).

Layer (cm)	Horizon	Description	TOC (g kg ⁻¹)	N (g kg ⁻¹)	D _b (g cm ⁻³)	RDW ^(a) (t ha ⁻¹)
0-10	A	Silt Loam	43.1	36.0	1.07	(14) + 3.99
10-20	A	Silt Loam	43.4	43.9	1.23	1.49
20-30	A	Silt Loam	29.0	29.0	1.24	0.57
30-40	Bh	Sand gravel+stones	19.7	21.0	1.27	1.07
40-50	Bh	Sand gravel+stones	8.60	10.1	1.31	0.25
50-60	Bh	Sand gravel+stones	7.40	9.5	1.43	0.01
60-70	Bh	Sand gravel+stones	8.30	6.6	1.48	-
70-80	Bh	Sand gravel+stones	10.1	7.3	1.54	-

Table 1: The brown podzolic soil profile from 0 to 80 cm depth was characterized by three horizons and described as Silt Loam from soil surface to 30 cm depth, and sand, gravel, and stones from 30 to the bedrock. Mean values of total organic carbon (TOC), total nitrogen (N), total bulk density (D_b), and RDW. (a) Root mass at the 0-10 layer include rhizome mass.

4.3.2 CO₂ production data

To estimate the soil CO₂ production we used the data of CO₂ concentration, soil temperature, and soil water content collected from days of the year (DOY) 1 to 283 of 2008. As the soil CO₂ concentration (Chapter 3) and the soil CO₂ efflux at soil surface (Chapter 4), the CO₂ production rates along the soil profile at both sample sites were high in summer and low in winter. Seasonally, CO₂ production rates varied from 0.2 to 9.7 gCO₂ m⁻² day⁻¹ in Winter, from 0.5 to 20.5 gCO₂ m⁻² day⁻¹ in Spring, from 0 to 38.5 gCO₂ m⁻² day⁻¹ in Summer, and from 0.7 to 24.2 gCO₂ m⁻² day⁻¹ in Autumn (Table 2).

Winter					
	pCO ₂ (0-10) (gCO ₂ m ⁻² day ⁻¹)	pCO ₂ (10-20) (gCO ₂ m ⁻² day ⁻¹)	pCO ₂ (20-40) (gCO ₂ m ⁻² day ⁻¹)	pCO ₂ (40-80) (gCO ₂ m ⁻² day ⁻¹)	TOT pCO ₂ (gCO ₂ m ⁻² day ⁻¹)
Min	0	0.2	0	-1.6E-15	0.2
Max	7	2.2	0.5	1.7E-15	9.7
Mean	1.3	0.9	0.2	4.8E-17	2.4
Spring					
Min	0.03	0.5	0	-4.2E-15	0.5
Max	15	5	0.5	4.3E-15	20.5
Mean	5.2	2.3	0.1	3.9E-17	7.6
Summer					
Min	0	0	0	-4.4E-15	0
Max	27	9	2.5	5.1E-15	38.5
Mean	8.7	3.6	0.2	5.7E-17	12.5
Autumn					
Min	0.03	0.7	0	-3.8E-15	0.7
Max	16.8	6.5	0.9	3.8E-15	24.2
Mean	8.3	3.9	0.3	9.2E-17	12.5

Table 2: Seasonality of minimum, maximum, and mean values of CO₂ production rates from the four layers of the soil profile. Also reported the total value of the production rates. Note that the negative values, corresponding with the precipitation events, were offset to zero, therefore not reported in this table.

Throughout the study period the CO₂ production rate was greater in the top layer than in the deeper layers. The layer 0-10 cm showed a CO₂ production that varied from 0 to 27.1 gCO₂ m⁻² day⁻¹, in the layer 10-20 cm varied from 0 to 9 gCO₂ m⁻² day⁻¹, in the layer 20-40 cm varied from 0 to 2.5 gCO₂ m⁻² day⁻¹, and in the deepest layer (40-80 cm) varied from -4.4×10⁻¹⁵ to 5.1×10⁻¹⁵ gCO₂ m⁻² day⁻¹ (Table 2). The CO₂ produced within the top 20 cm closely followed diurnal trends of soil temperature, and solar radiation, whereas at deeper soil depth such relationship became less apparent (Figure 2).

Overall, the sum of the production rates predicted in each layer accounted for 86% of the variance in surface CO₂ efflux estimated by the gradient approach in Chapter 3 (Figure 3a). However, surface flux more closely followed changes of CO₂ production in the top 20 cm of the soil profile. Due to the influence at soil surface of advective forces caused by wind speed, atmospheric pressure changes, and rapid changes of soil diffusivity at soil surface (Risk et al. 2001), the correlation between soil CO₂ efflux and CO₂ production at 0-10 cm was lower (about 78%) than the layer 10-20, which was about 95% (Figure 3b,c). Finally, the efflux estimated at soil surface was not a good indicator of the low CO₂ production at the deep layers. The correlation between soil surface efflux and CO₂ production at 20-40 cm was negative and very weak ($R^2=0.03$), while was completely absent with the layer 40-80 cm (see Figure 3d).

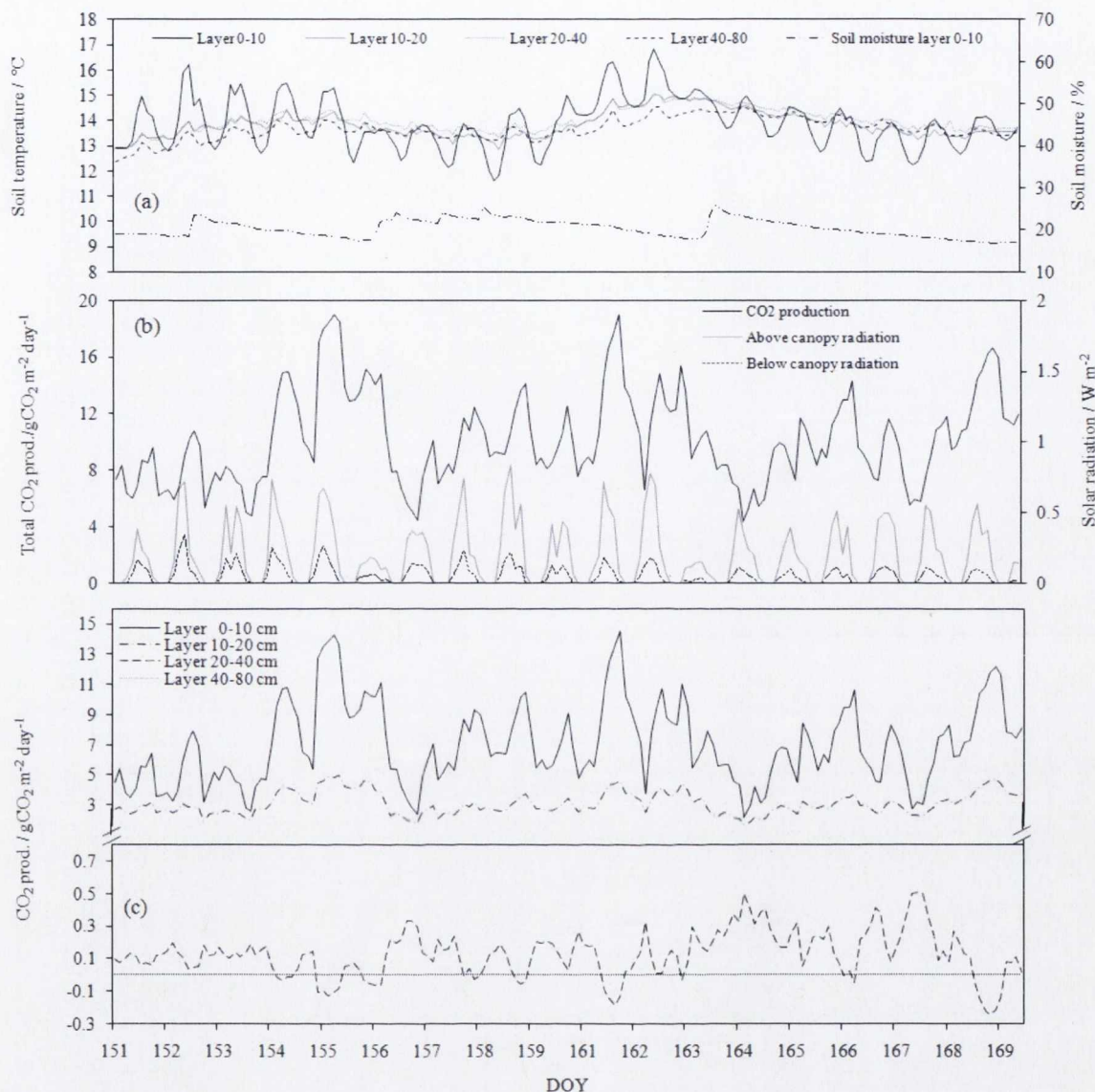


Figure 2: Influence of the soil temperature, soil moisture and solar radiation on the hourly mean values of CO₂ production rates from DOY 151 to 169 in 2008. (a) Soil temperature from 10 to 80 cm depth, and soil moisture at 10 cm depth, (b) total CO₂ production, and above and below canopy solar radiation, and (c) contribution of CO₂ production from the 0-10, 10-20, 20-40, and 40-80 cm layer. Note that in the plot (c) the y-axes scale differs.

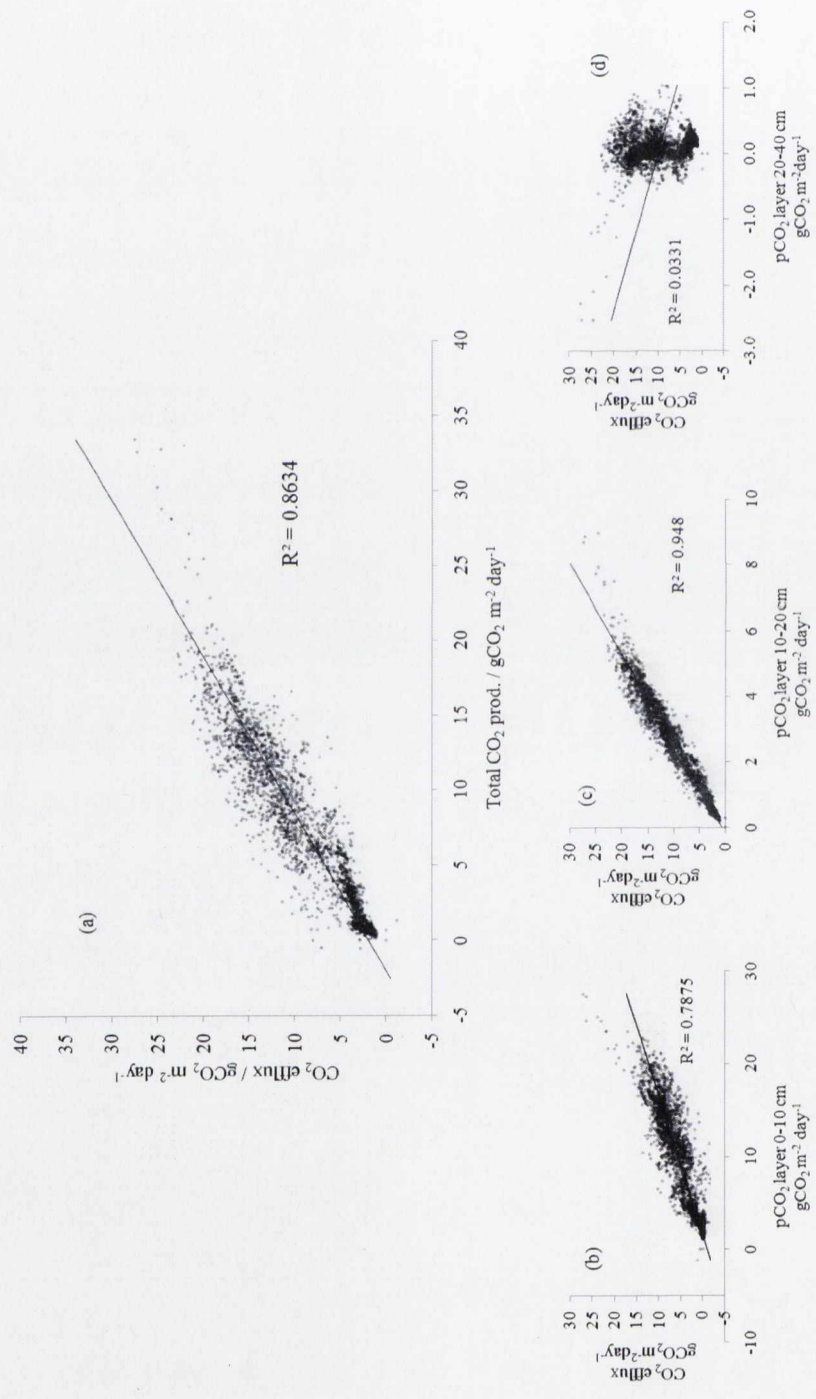


Figure 3: Relationship between the estimated soil CO₂ efflux (Chapter 4) and the calculated production rates. The graphs show the mean hourly values from DOY 1 to 283 in 2008 of: (a) estimated soil CO₂ efflux vs. total soil CO₂ production rates at soil surface, (b) estimated soil CO₂ efflux vs. soil CO₂ production rates from the 0-10 cm layer, (c) estimated soil CO₂ efflux vs. soil CO₂ production rates from 10-20 cm layer, and (d) estimated soil CO₂ efflux vs. soil CO₂ production rates from 20-40 cm layer.

4.3.3 Relationship between CO₂ production rates and soil moisture

Mean soil water content (θ), which was affected by rainfall events, ranged from 15.7 to 21.1% in the top layer, from 11.5 to 21.5% in the 10-20 layer, from 8.5 to 19.1% in the 20-40 cm layer, and from 6.8 to 16.6% in the 40-80 cm layer. Although on a daily basis the CO₂ production rates at all soil depth were not well correlated to θ , at weekly basis the CO₂ production in the 0-10 cm and 10-20 cm layer was negatively correlated to θ with an R^2 of about 0.44 and 0.42 respectively (Figure 4a, b). Moreover, at the 20-40 cm and 40-80 cm the CO₂ production was positive correlated to θ although their correlation did show very weak values (Figure 4c, d).

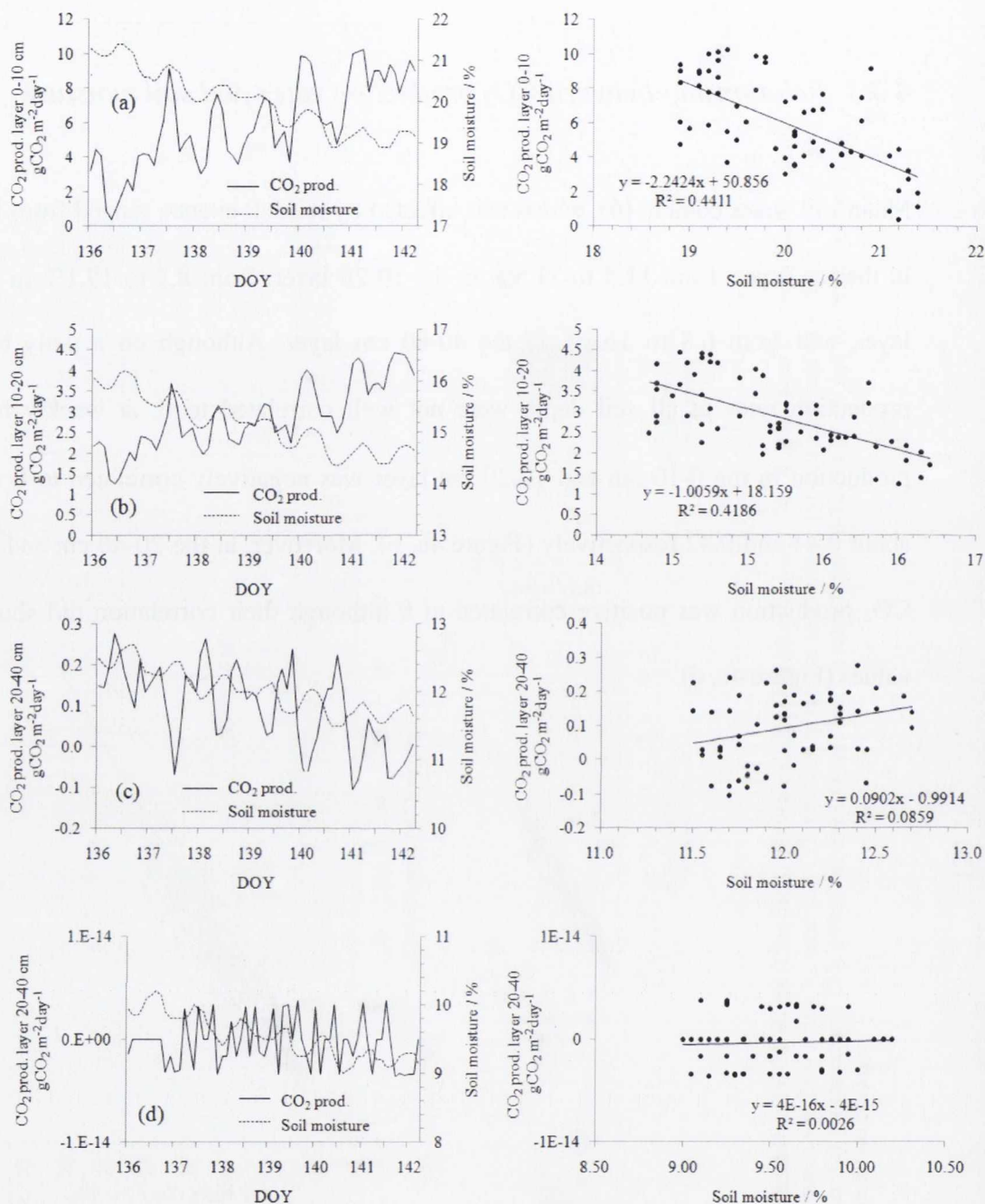


Figure 4: Influence of the soil moisture on the soil CO₂ production rates throughout the soil profile. The graphs show the time series of hourly mean values from the 16th to 22nd of May of: (a) soil CO₂ production and soil moisture at the 0-10 cm layer, (b) soil CO₂ production and soil moisture at the 10-20 cm layer, (c) soil CO₂ production and soil moisture at the 20-40 cm layer, and (d) soil CO₂ production and soil moisture at the 40-80 cm layer. Also shown on the right the respective correlations plots.

4.3.4 Relationship between CO₂ production rates and soil temperature

Production estimated within each layer was correlated to temperature measured throughout the profile. The temperature sensitivity expressed using equation [6] showed a Q_{10} that decreased from the soil surface to the bottom of the soil profile. In particular the top layer (0-10 cm) showed a high Q_{10} of 10.2, the 10-20 cm layer a Q_{10} of about 6.3, the layer 20-40 cm of 1.8, and the deeper layer (40-80 cm) a very weak Q_{10} of about 0.02 (Figure 5a, b, c, d). The temperature regression function fitted to the data for CO₂ production at the top layer (0-10 cm) showed a lower correlation ($R^2=0.33$) than in the layer of 10-20 cm ($R^2=0.64$). Moreover, at the deeper layers, 20-40 cm, and 40-80 cm, the exponential function showed very weak correlation values of about 0.04 and 0.6, respectively (Figure 5).

The residuals of the regression model production vs. temperature for the 0-10 cm layer (Figure 5a) were best explained by the soil water content (Figure 6):

$$\text{Residuals}_{\alpha_{(0-10)}} = -0.5389 \times \theta_{(0-10)} + 13.539 \quad [7]$$

By adding the water content linear function of the residuals (Eqn [7]) to the entire dataset of CO₂ production rates at 0-10, the CO₂ production-temperature regression model improved its predictive power R^2 from 0.33 to 0.4 with a Q_{10} of 4.2 (Figure 6).

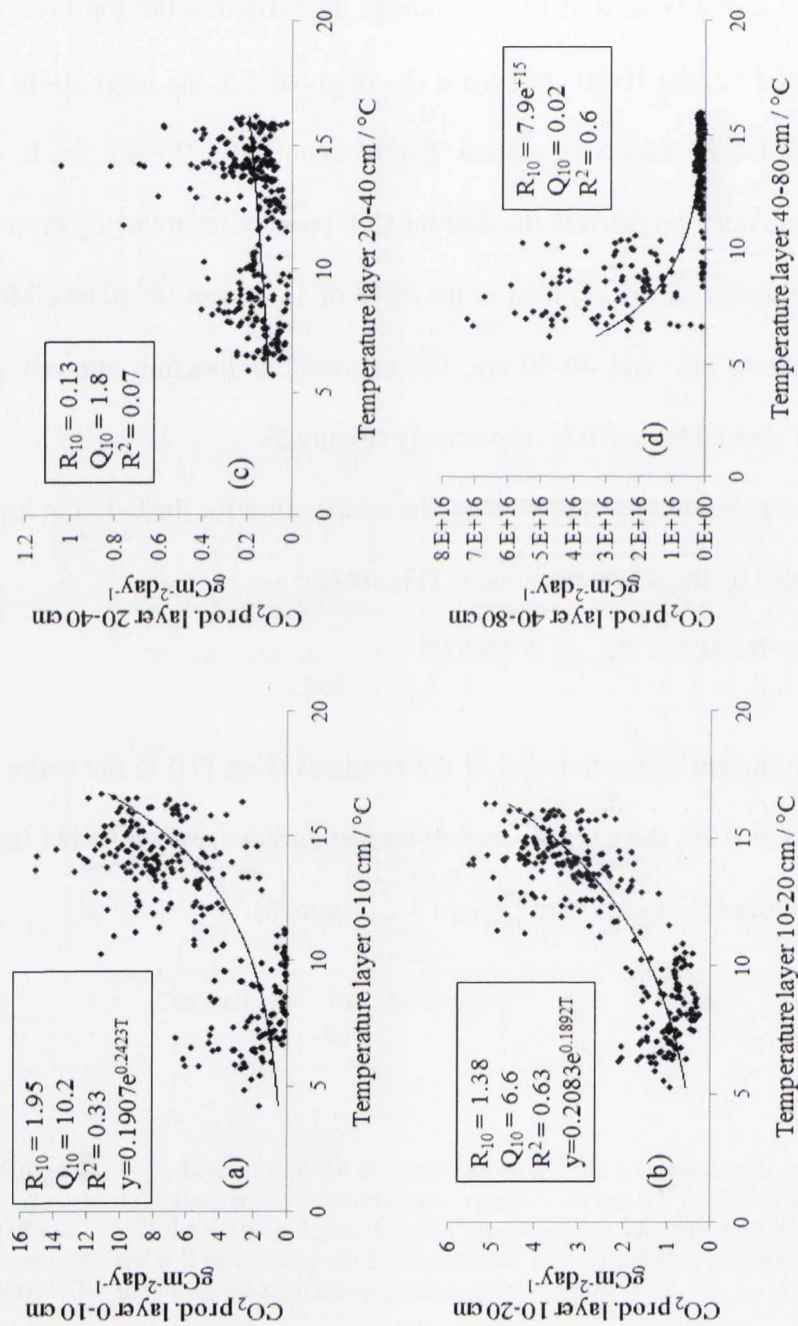


Figure 5: Influence of soil temperature on CO₂ production rates throughout the soil profile. The graphs show the relationship between daily mean values from DOY 1 to 283 in 2008 of: (a) soil CO₂ production and soil temperature in the layer 0-10 cm, (b) soil CO₂ production and soil temperature in the layer 10-20 cm, (c) soil CO₂ production and soil temperature in the layer 20-40 cm, and (d) soil CO₂ production and soil temperature in the layer 40-80 cm. Also shown the respective temperature sensitivity value (Q_{10}), the value of CO₂ production at 10 °C (R_{10}), and the correlation fit (R^2) calculated fitting the data with Eqn. [6]

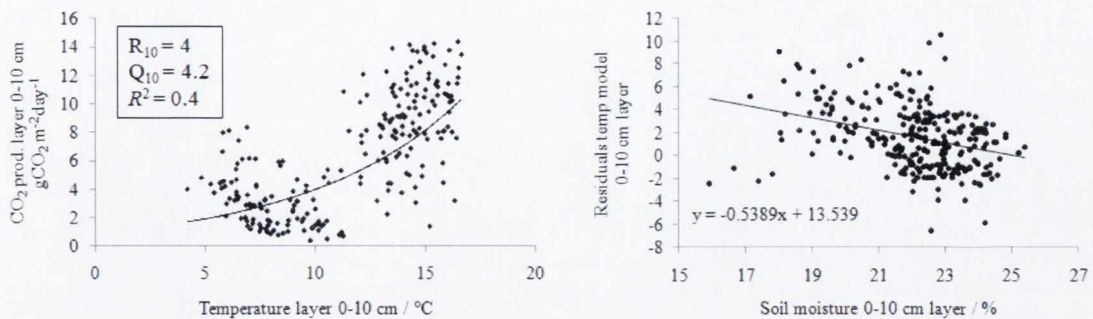


Figure 6: Soil CO₂ production rates from the layer 0-10 cm as a function of soil temperature. (a) soil CO₂ production corrected by the moisture vs. soil temperature in the layer 0-10 cm. Also shown the temperature sensitivity value (Q_{10}), the value of temperature at 10 °C (R_{10}), and the correlation fit (R^2) calculated fitting the data with Eqn. [6]. On the right the plot of the residuals errors term of the graph 5(a) as a function of the soil moisture at the 0-10 cm layer.

4.4 Discussion

Generally, soil organic matter content (SOM) and root density decrease with increasing depth (Jobbágy and Jackson 2000). As a result, also the CO₂ production rate within the soil profile, which varies among ecosystems, tends to decrease with increasing depth (Ino and Monsi 1969; Hashimoto and Suzuki 2002). Yano and Kayama (1975), in a natural grass dominated by *Miscanthus × giganteus* in northern Japan, reported that rooting depth was about 120 cm. Neukirchen et al. (1999), studying the spatial and temporal distribution of the root system in *Miscanthus × giganteus* in Western Germany, found that in a sandy loam soil the vertical distribution of the roots reached a maximum depth of 250 cm. However, they also reported that, although *Miscanthus* builds up a root system at depth, the 30% of the root biomass was constrained in the top 30 cm of soil profile. A possible explanation of these disagreements among studies is the different of soil conditions (soil compaction layers, water holding capacity, and nutrient availability) which are known to have a great effect on root growth

(Boone, 1986; Donald et al., 1987; Bengough and Mullins, 1990; Passioura and Stirzaker, 1993; Cornish, 1993; Wolfe et al., 1995). In our site, characterized by a silt loam horizon in the top 30 cm, and a sandy gravel horizon from 30cm to the bedrock, we found that the whole *Miscanthus* rooting system was confined within 60 cm of soil depth, and that about 82% of the root biomass was confined in the top 30 cm. As a result, over the four seasons we found that the top layer (0-10 cm) contributed approximately from 0 to 81% (mean value 59%) of total soil CO₂ efflux, the 10-20 cm layer from 17 to 96% (mean value 35%), the 20-40 cm layer from 5 to 48% (mean value 6%), and the bottom layer (40-80 cm) made a negligible contribution. Similarly to the soil surface CO₂ efflux (Chapter 3), the CO₂ production changed seasonally at all soil depth showing a greatest production during the growing season. Moreover, rates of CO₂ production mostly increased with soil temperature throughout the profile, although at the bottom layer the production was too weak to permit a correlation with the soil temperature.

Top layer CO₂ production ranged from 0 to 7.4 gC m⁻² day⁻¹, with a mean value of 1.5 gC m⁻² day⁻¹. Considering the rate of mean annual C of aboveground biomass residues falling to the ground (2.9 gC m⁻² day⁻¹), this indicate that the top layer, depending by the weather conditions, could represent a significant transient source or sink of carbon on the seasonal basis. However, assuming that the 0-10 cm layer remains at steady state condition over long term, no more than half of the CO₂ production can come from decomposition of the SOM. Therefore, root, mycorrhizal respiration, root exudates, and mycorrhizal C must comprise the other half or more of the CO₂ produced in the top layer. Exploring deeper soil layers, the 10-20 cm layer contributed from 0 to 2.4 gC m⁻² day⁻¹ to the total surface CO₂ efflux, the layer 20-

40 cm from 0 to $0.7 \text{ gC m}^{-2} \text{ day}^{-1}$, and the deepest layer (40-80 cm) from 0 to $5.1 \times 10^{-15} \text{ gC m}^{-2} \text{ day}^{-1}$.

Although shallow soil contains much carbon, a significant amount of organic carbon is also present in the deeper soil. Jobbágy and Jackson (2000) reported that more than half of the organic carbon present in the top 1 m of soil is generally found below 0.2 m. Because the decomposition of organic matter is very sensitive to temperature, the temperature response of soil organic carbon decomposition in deep soil is a critical issue for our understanding of global warming and its impact. Hirsch et al. (2002), measuring deep-soil respiration directly in the BOREAS northern black spruce site in Canada, found that deep-soil respiration increased linearly with temperature within the top 0.5 m of soil, with a slope of $0.2 \text{ kgC ha}^{-1} \text{ day}^{-1} \text{ }^{\circ}\text{C}^{-1}$. Risk et al. (2002) also found positive relationships between soil temperature and subsurface CO_2 production at four sites in eastern Nova Scotia, Canada. Davidson et al. (2006) reported that in a mixed deciduous forest in Massachusetts USA, the CO_2 production rates in a soil profile of about 65 cm depth, characterized by four soil horizons (*O*, *A*, *B*, and *C*), were correlated to temperature by a Q_{10} varying from 2.3 to 1.5. As for the above studies, we found that the soil CO_2 production rates in the top three layers from 0 to 40 cm depth were positively correlated to the soil temperature (Figure 2, 4), whereas due to the weak signal no trend was found at the 40-80 layer. However, in contrast with other studies that reported an increasing Q_{10} from soil surface to the deeper soil layers (Davidson et al 2006; Hashimoto et al., 2007), we found that in our site the Q_{10} of the CO_2 production rates decreased throughout the soil profile from 10.2 to 0.02. Generally, the high Q_{10} of the production of CO_2 in the top soil layer results from the covarying effects of temperature, moisture and solar radiation on multiple

processes (Davidson et al 1996, 2006). A Q_{10} value at the top layer might also be related to soil physical events such as limited diffusivity of the soil matrix after rainfall events (Millington, 1959; McCarty et al., 1999), wind pressure changes (Renault et al., 1998; Massman et al., 1997), or simultaneous vertical transport of heat and water (Fang and Moncrieff, 1999). Generally the biological production of CO_2 , and the natural movement throughout the soil profile, is modified by the occurrence of these events, making the soil profile CO_2 efflux and production analysis more complex. In our site, during the rainfall events the soil CO_2 concentrations in the top soil layer, and therefore the production rates, showed a great fluctuation which affected, with negative values, the seasonal budget of CO_2 production rates. However, unlike other studies which removed the negative production rates (DeJong and Schappert, 1972; Risk et al., 2002; Hashimoto et al., 2007), we decided to show their effects on the Q_{10} (Figure 5), and also to show how, by adding a soil moisture function to the 0-10 layer CO_2 production results (Figure 6), the relationship soil temperature- CO_2 production improved the R^2 from 0.34 to 0.4 with a reduction of Q_{10} from 10.2 to 4.2.

The sum of the production rates calculated in each layer accounted for 86% of the variance in surface CO_2 efflux estimated by the gradient approach (Figure 3a). In this respect, the use of high temporal resolution measurements of CO_2 concentrations at soil surface was essential to determine CO_2 production in the top layer. Ideally, concentrations at all depths (from 0cm to the bottom of the soil profile) should be used to estimate CO_2 production. An overestimation of CO_2 concentrations at the top of a layer can cause the underestimation of the CO_2 concentration gradient, as well as of the CO_2 efflux. Consequently an underestimation of the production in the top layer would cause an overestimation of the deeper layers production. For

this reason, rather than estimating the CO₂ production of the top layer (0-10 cm) from the difference between soil chamber efflux measurements and the production values of the deeper soil profiles (Davidson et al 2006; Hashimoto et al., 2007), or by using soil profile CO₂ concentrations measured in the proximity of the soil surface (Risk et al., 2002), we estimated the top layer CO₂ production directly using CO₂ concentrations measured at soil surface. As a result, surface efflux was a good indicator of changes of subsurface CO₂ production in the two top layers $R^2 = 0.78$, and 0.98 (Figure 3b, c). Finally, because the CO₂ production rates from each soil layer was calculated using measured CO₂ concentrations, and the CO₂ efflux was estimated using CO₂ concentrations estimated by a quadratic function model (Chapter 4), this results represent an additional validation of the quadratic function model to estimate the temporal trends of CO₂ concentrations in the soil profile.

At the 0-10 cm, and 10-20 cm layers the CO₂ production rate inversely increased with the soil water contents (Fig. 4a, b). Generally, during the initial stages of the rainfall events water infiltration filled the pores replacing the soil gases and creating peaks of CO₂ concentration which shifted downward through the profile (Chapter 2). However, after these initial changes in CO₂ concentrations, the high soil water content condition, which interrupts the open-air void pathway to the atmosphere, appeared to inhibit the CO₂ production in the top 20 cm depth of the soil profile. Vice versa, in the 20-40 cm layer the CO₂ production was positively correlated to the soil moisture content. Soil at that depth was generally less wet than the shallower soil, therefore an increase in soil water content probably stimulated the soil CO₂ production.

4.5 Conclusion

Measurements of soil profile CO₂ production rates with the use of soil diffusivity models still remain a challenging approach. The effects of the environmental factors such as water content, and temperature, which alter the movement of the CO₂ throughout the soil profile, as well as the biological components of soil respiration, make the measurement of CO₂ production among the soil profiles difficult to define. However, the partition of soil CO₂ effluxes within the soil profile is a powerful tool for the assessment of season patterns of subsurface CO₂ production and its dependence to the main environmental drivers.

Calculated values of soil CO₂ production showed that over four seasons in 2008 the top layer (0-10 cm) contributed on average 59% of total soil CO₂ efflux, the 10-20 cm layer 35%, the 20-40 cm layer 6%, and the bottom layer (40-80 cm) had a negligible contribution. The production of CO₂ appeared to be strongly controlled by the temperature, despite the soil water content changes affected this relationship. In particular CO₂ production rates in the top 20 cm showed a negative relationship with soil water content, whereas a weak positive relationship was found in the deeper soil layers. Generally, in the shallow soil layers the CO₂ production was higher in dry conditions and lower in wet condition, whereas in deeper layers, although the weak R^2 , this relationship appeared to be inverted.

The temperate sensitivity of CO₂ production varied across the soil profile ranging from 10.2 at the top to 0.02 at the bottom layer. However, by correcting the CO₂ production from the top layer to exclude the effect of soil moisture changes the Q_{10} value showed a reduction from 10.2 to 4.2 with an improvement of the R^2 .

Overall this study confirmed how important it is to investigate soil subsurface processes in order to improve our knowledge on soil respiration. To our knowledge this is the first time that CO₂ production rates have been calculated using a technique able to measure high-temporal resolution soil profile CO₂ concentrations including soil surface measurements.

Chapter 5

Conclusions and perspectives

To synthesize the main findings of my research, I will return to the original objectives stated in the outline of the thesis. Firstly, I will discuss whether, and by what characteristics, the soil diffusion chambers represent a good and new technique for measuring CO₂ concentration in soil profile. Secondly, I will discuss how we assessed soil CO₂ efflux and the relative contribution of soil CO₂ production by different soil profile layers. Thirdly, synthesizing the results of my research, I will indicate the advantages of using soil profile approach, as well as our technique for studying soil respiration. Finally, I will point out future perspectives that may develop from this study.

5.1 Testing the objectives

5.1.1 Advantages of using soil diffusion chambers technique

The soil diffusion chambers were designed to semi-continuously measure CO₂ concentrations within the soil profile. Their development aimed to combine the advantages of some of the

methods developed by previous soil profile gradient studies, and to overcome some of their disadvantages. In essence, the fundamental characteristics of the technique are:

- (i) The use of static cylindrical HDPE chambers which allowed the exchange of gas between the sampling device and the soil, and as described in previous studies, allowed stable and reliable measuring conditions from soil surface to 80 cm depth.
- (ii) The use of the a PVDF gas permeable membrane which provided a physical barrier to separate the gas phase and the surrounding soil/water, avoiding the probability of mass gaseous flow in the soil matrix from undefined depths, the distortion of the gas profile in the soil, and allowing reliable measurements in wet or flooded soil conditions The use of the PVDF membrane, tested in laboratory, and used for the first time in soil profile gas measurement techniques, guaranteed a good diffusivity of soil CO₂ into the chambers, and a quick equilibration time of the CO₂ between the inner volumes of the chambers and the soil matrix. Moreover, the PVDF membrane has repellent properties that prevent the formation of a bacterial biofilm on the surface of the chambers (Yabune *et al.*, 2005), and therefore the production of biogenenic gases able to affect the normal CO₂ production in the soil profile (Rothfuss and Conrad, 1994).
- (iii) The adoption of a closed loop gas circulation between the soil surface and the belowground diffusion chambers which allowed high temporal resolution measurements of the CO₂ concentrations profile aboveground, and limited the creation of pressure differentials within the diffusion chamber, and between the diffusion chamber and the surrounding soil matrix (Fang and Moncrieff, 1998 Gut *et al.*, 1998, DeSutter *et al.*, 2006).

- (iv) The inclusion of the whole chamber in a metal and plastic mesh which provided a physical protection from micro and macrofauna, and the preservation of the diffusion properties of the PVDF membrane throughout the study.

5.1.2 *Assessing soil respiration using a gradient-based approach*

Gaseous movement from soil to the atmosphere is primarily controlled by two processes: (i) the mass flow, and (ii) the molecular diffusion. Mass flow controls the CO₂ movement by a pressure gradient where CO₂ moves from soil zones with high pressure to zones with low pressure. Molecular diffusion regulates the CO₂ movement along a concentration gradient, where the CO₂ molecules migrate from zone of higher concentrations to zone of lower concentrations. Therefore, we assessed the soil CO₂ efflux using the Fick's first law equation.

By using the high temporal resolution CO₂ concentrations profile, soil temperature, soil water content, and soil physical characteristics measurements from soil surface to 80 cm depth, we assessed the CO₂ concentration gradient ($\Delta C/\Delta Z$) and the soil diffusivity (D_s). The $\Delta C/\Delta Z$ along the five measuring points of the soil profile had a characteristic quadratic shape skewed towards the bottom of the profile, and generally showed maximum CO₂ concentrations value at 40 cm depth. Therefore, the best fit to the data was given by a quadratic model, which well described the natural behavior of $\Delta C/\Delta Z$ during most of the soil and atmospheric conditions, and fitted the measured CO₂ concentrations throughout the study with a mean absolute percentage error of 24.3%. The soil-specific D_s value for each soil profile measuring point was estimated by using the Millington-Quirk model. To account for

the spatial variation of texture properties in the soil profile, and non uniform vertical distribution of soil water content, we calculated the effective soil profile D_s based on harmonic averaging of individual diffusivities of each profile layers. Therefore resembling the slope of a linear regression between the individual D_s of each layer and the soil profile depth.

Overall, the mean values of soil CO_2 efflux estimated with the gradient-approach were similar to the values measured by the automated surface chamber. A point of interest in these results was the use of a diffusion chamber designed for measuring at soil surface which allowed us to accurately measure the CO_2 concentrations at soil surface, even in presence of air turbulence or rainfall events, and to have a better estimate of $\Delta C/\Delta Z$ at the boundary layer between soil surface and atmosphere.

The CO_2 production rates from the soil was estimated by partitioning the profile in four layers (0–0.1 m, 0.1–0.2 m, 0.2–0.4 m, and 0.4–0.8 m), and assuming that the CO_2 concentrations profile conditions remained close to a steady state over time. In essence, the gradient of CO_2 efflux between adjacent layers indicated the contribution of CO_2 production from each layer. In other words, the production at each depth was calculated from the difference between the outward output flux from a generic layer minus input flux from a layer below (Davidson and Trumbore, 1995).

5.1.3 Advantages of using soil profile gradient approach in soil respiration studies.

Generally the interest in soil profile CO_2 efflux studies lies in understanding the factors

controlling the belowground variability of soil respiration, the processes that control CO₂ production and emission, and to identify localized sources and potential sinks in the soil profile.

By carrying out this profile study we found that:

- (i) At a daily basis the soil temperature and water content appeared to be the primary environmental drivers of the CO₂ concentrations throughout the soil profile, although in deep soil the effects of soil temperature were more attenuated. However, CO₂ concentrations throughout the soil profile were always an order of magnitude higher than in the atmosphere resulting in a constant concentration gradient from deep layers to the atmosphere.
- (ii) As for the CO₂ concentrations, the estimated soil CO₂ efflux rates appeared to be strongly regulated at a daily basis by soil temperature and soil moisture. In particular, during the growing season the apparent differential responses of soil CO₂ efflux to soil warming and cooling led to a diurnal hysteresis behavior of the soil respiration, and a phase shift between the daily peaks of CO₂ efflux and soil temperature (maximum time lag of approximately three hours) which reduced the daily correlation between the CO₂ efflux and the soil temperature.
- (iii) At weekly and seasonal basis soil temperature remained the main driver of soil respiration. However, due to rainfall events the fluctuations of soil water content negatively affected the temperature-respiration relationship. Moreover, during synoptic weather conditions the wind speed, and atmospheric pressure changes, played a fundamental role on controlling the soil CO₂ emissions.

- (iv) The temperature sensitivity of soil respiration varied from 4.3 to 7.6 in relation to the soil profile temperature used. In addition, the correlation R^2 with the temperature improved when soil profile temperatures between 10 and 40 cm depth were considered.
- (v) Similarly to the soil surface CO_2 efflux, the CO_2 production changed seasonally throughout the soil profile showing a greatest production during the growing season. In particular, the soil CO_2 production rates in the top three layers from 0 to 40 cm depth were positively correlated to the soil temperature, whereas due to the weak signal no trend was found at the 40-80 layer. Moreover, we found that the Q_{10} of the CO_2 production rates decreased throughout the soil profile from 10.2 to 0.02. The high Q_{10} of the production in the top soil layer resulted from the confounding effects of soil moisture linked to the limited diffusivity of the soil matrix after rainfall events. By correcting the CO_2 production results of the top soil layer by a soil moisture function the empirical temperature model of the relationship temperature- CO_2 production improved the R^2 from 0.34 to 0.4 with a reduction of Q_{10} from 10.2 to 4.2.
- (vi) Top layer CO_2 production ranged from 0 to $7.4 \text{ gC m}^{-2} \text{ day}^{-1}$, with a mean value of $1.5 \text{ gC m}^{-2} \text{ day}^{-1}$. Considering the mean annual C of aboveground biomass residues falling to the ground ($2.9 \text{ gC m}^{-2} \text{ day}^{-1}$), depending by the climatic conditions the top layer (0-10 cm depth) of the soil profile could represent a significant transient source or sink of carbon on the seasonal basis. However, the top layer contributed approximately 59% of total soil CO_2 efflux, the 10-20 cm layer 35%, the 20-40 cm layer 6%, and the bottom layer had a negligible contribution. Due to the disturbances of rainfall events, atmospheric pressure, and wind speed, the top layer CO_2 production was more variable

than deeper layers production.

- (vii) At the 0-10 cm, and 10-20 cm layers the CO₂ production rates were inversely correlated to soil water content changes. However in the 20-40 cm layer the CO₂ production was positively correlated to the soil moisture content.
- (viii) Finally, the sum of the production rates calculated in each layer accounted for 86% of the variance in surface CO₂ efflux estimated by the gradient approach. Moreover, the surface efflux closely followed CO₂ production rates of the layer 0-10 cm ($R^2 = 0.78$) and of the layer 10-20 cm ($R^2 = 0.98$).

5.2 Perspectives

1. These results would certainly benefit from the application of continuous carbon stable isotope studies, and from manipulation experiments, such as girdling or controlling temperature. Following a change in cropping practice between C₃ and C₄ plants the isotopic signature of plant input to soil provides an appropriate method for studying plant-soil-atmosphere carbon dynamics. However, tracing the fate of carbon into specific biological soil components is still difficult. Although it is recognized that the C isotopic composition of soil respired CO₂ is the same as that of the biological sources, under the steady-state production/diffusion conditions in the soil profile the isotopic composition of the CO₂ measured at soil surface generally shows a gradual change from the isotopic value of their biological sources. Nowadays the research on the isotopic composition of soil CO₂ has successfully demonstrated that the CO₂ that diffuse from the soil is enriched by 4.4 ‰ comparison to its biological source due to

the quicker diffusion of $^{12}\text{CO}_2$ than the $^{13}\text{CO}_2$. This means that the measurements of the isotopic composition of respired CO_2 at soil surface and within the soil profile require the development of new methods and or techniques able to do not disturb the natural steady state soil CO_2 concentration and $\delta^{13}\text{C}$ in the soil profile. Recently, Nickerson and Risk (2009) reported the use of open or closed chambers, which impose a non-steady state environment, can affect isotopic measurements by up to 2 ‰. They also reported that this bias is not constant but can change with the soil properties such as porosity, moisture, diffusivity, production rate, and concentration gradient. Although, the magnitude of error might be acceptable in some circumstances, it could be a problem if small differences in source signature are being exploited.

During this PhD study, by using the soil profile diffusion technique in combination with a cryogenic H_2O and CO_2 trapping-purification line, I attempted the development of a gas equilibration system able to collect, at soil surface, soil CO_2 from the belowground diffusion chambers, whilst maintaining the natural steady-state conditions. Due to time and financial constraints of my PhD, I had only the possibility to complete the preliminary tests which showed promising results in term of stability in measuring the ^{13}C values of deep soil CO_2 under the equilibration and diffusion soil processes. However, these preliminary results suggest a valuable perspective that could develop from the use of the soil diffusion chamber and from the results of this study. The hysteresis in soil respiration observed in this dissertation are generally attributed to the production and translocation of photosynthate from the leaves, through the phloem and to the roots and associated microbes. Because the sensitivity of

respiration responding to photosynthesis is small, the above time lag and the correlation between respiration and photosynthesis is often suppressed by more sensitive drivers such as temperature and moisture, thus is not easily detected. For these reasons, the use of techniques such as soil diffusion chamber, which permit continuous and precise measurements of soil CO₂ concentration, combined with continuous stable carbon isotope analysis of CO₂, would clearly be an advantage to explore the linkage between photosynthesis and soil activity, as well as to partition soil respiration into its autotrophic and heterotrophic components.

2. The use of diffusion chambers for soil profile gradient measurements of soil respiration combined with the estimation of the accumulation and depletion of available carbon substrate would represent a new trend for examining the effects of environmental factors on carbon pool sizes.
3. Finally, the use of soil diffusion chambers would provide important additional information on soil profile CO₂ storage to improve the estimation of ecosystem respiration in overstory and understory flux measurements using the eddy covariance method.

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