

The biogeochemical processes controlling the soil carbon cycle at the hillslope scale.

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List of abbreviations and symbols

^{137}Cs	Isotope of Cesium with a molar mass of 137 g/mol
1-D	One dimensional
2-D	Two dimensional
3-D	Three dimensional
a.o.	Among other things
b	Slope of the Campbell (1974) soil water retention curve model between -100 and -500 cm H ₂ O water suction [-]
BD	Soil bulk density [kg m ⁻³ or g cm ⁻³]
BP	Before present
Bq	Becquerel (SI derived unit of radioactivity)
C	Carbon
c.	Circa (meaning “about”)
CO ₂	Carbon dioxide
CWEOC	cold water-extractable OC
d	soil depth at which the sharpness of the curve changes due to a diffusion barrier [cm]
DGPS	Differential global positioning system device
DIC	Dissolved inorganic carbon
DOC	dissolved organic carbon
DOY	Day of year
DPM	Decomposable plant matter
D _s	Diffusivity of CO ₂ in soil [m ² s ⁻¹]
e.g.	Exempli gratia, meaning “for exemple”
FDR	Frequency domain reflectrometry
Fe _{DCB}	crystalline and poorly crystalline Fe oxyhydroxides

GHG	Greenhouse gas
GLS	Generalized Least Square
GPR	Ground Penetrating Radar
ha	Hectare = 10 000 m ²
HUM	Humus
i.e.	Id Est , meaning “that is”
IC	Inorganic carbon
IPCC	Intergovernmental Panel on Climate Change
IRGA	Infra-red gas analyzer
ln	Natural logarithm
LOC	Labile OC
ME	Model error
Mg	Mega grams = 10 ⁹ grams
MPOC	Mineral-protected OC
NDIR	Non-dispersive infra-red
NPP	Net Primary Production
OC	Organic carbon
OM	Organic matter
Pg	Pega grams = 10 ¹⁵ grams = 10 ⁹ tons = 1 Mega tons (Mt)
ppm	Parts per million = 10 ⁶ v%
PTFE	polytetrafluoroethylene
Q ₁₀	Temperature sensitivity of organic carbon decomposition [-]
R ²	Regression coefficient

Rs	Soil heterotrophic respiration
S	Percentage of mineral soil with particle size > 2 μ m (= 100 - clay content)
SD	Standard deviation
Si _{ox} , Al _{ox} , and Fe _{ox}	Concentration of Al, Fe and Si in the oxalate-extractable solutions
StaOC	Stable organic carbon
SWR	Soil water retention
T	Temperature [°C]
TDR	Time domain reflectrometry
TOC	Total organic carbon
t-test	Student inference test
V%	Volumic percentage = 10 ⁻⁶ ppm
VWC	Volumetric water content [m ³ m ⁻³ or cm ³ cm ⁻³]
WFPS	Water filled pore spaces [m ³ m ⁻³ or cm ³ cm ⁻³]
yr	Year
γ_1 and γ_2	parameters which characterize the sharpness of the curve of the soil CO ₂ concentration profile [cm ⁻¹]
$\delta^{13}\text{C}$	Stable isotopic signature of carbon
$CO_{2,\infty}$	fitted asymptotic value of the CO ₂ concentration at infinite depth [%]
z	Soil depth [cm]
ε_{100}	Soil air-filled porosity at -100 cm water succion [m ³ m ⁻³]
ε	Soil air-filled porosity [m ³ m ⁻³]
$\emptyset$	Total soil porosity [m ³ m ⁻³]
μ	10 ⁻⁶

List of peer-reviewed publications

Published

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1. Introduction

1.1. Soil carbon: forms and turnover

1.1.1. Carbon sources in soils

The soil is a complex system which forms in the Regolith, i.e. the critical zone where weathering rocks (or any other mineral substrate) meet life. Hence, soils result from the combination of the weathering of soil minerals (coming from the parent material), the biological decomposition of materials from living origins at the interface with the biosphere, and the physical mixing of both these inorganic and organic components (e.g. Brantley et al., 2007; Stockmann et al., 2011).

Soils contain organic matter (OM), which is a mix of detritus from different living origins called primary sources (i.e. vegetal) and secondary sources (a.o. animals and microbes), which have been decomposed to a molecular state (e.g. Baldock et al., 2000). According to its scientific definition (Baldock et al., 2000), soil OM does not include non-decayed plant and animal tissues, partial decomposition products, nor living soil biomass (McCarthy et al., 1990). Soil OM has heterogeneous sources, impacting its chemical and physical composition, and its functioning (Baldock et al., 2000). Soil OM is mainly composed of colloidal organic substances containing acidic functional groups and N containing groups (amino acids, peptides, and proteins, and nitrogenous polymers), as well as *quinone* structures of lignin (e.g. Baldock et al., 2000; Flaig

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et al., 1975; Schnitzer, 1991; Stevenson et al., 1982). Hence, the main components of soil OM are carbon and nitrogen.

In addition, soil inorganic carbon (IC) is found in some soils as soil carbonates. Soil carbonates may have a variable mineral structure and chemical composition: this can be presented as calcite and aragonite (CaCO_3), magnesite (MgCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$), which are each characterized by a specific solubility (Appelo and Postma, 1994). Three main origins explain the presence of carbonates in soils. First, detrital carbonates are inherited from soil parental material (Rommens et al., 2005; Kraimer and Monger, 2009). Second, pedogenic or authigenic carbonates may be created during a pedogenic processes. Pedogenic carbonates are colloquially known as “Caliche” (Serrano-Ortiz et al., 2010; Schlesinger et al., 1985; 2009) or are sometimes called recrystallized carbonates (Gocke et al., 2012). Third, anthropogenic carbonates such as lime amendments may be applied to agricultural soils to control the soil pH (Biasi et al., 2008; Kraimer and Monger, 2009).

Hence, C is present in soils in both organic and inorganic forms. Each of these two types of molecules can be either in a solid or liquid state. Hence, soil contains organic C (OC), dissolved organic C (DOC), inorganic C (IC), and dissolved inorganic C (DIC).

1.1.2. Organic carbon dynamics and biotic CO_2 emissions

Through the metabolic pathway of respiration, soil micro-organisms use soil OC as a substrate and induce its oxidation in a mineral form, i.e. CO_2 (e.g. Bruggemann et al., 2011; Lal and Bruce, 1999). Hence, soil heterotrophic respiration can be used as an indicator both of the soil OC persistence (e.g. Gregorich et al., 1994) and of the rate of C loss from the soil to the atmosphere. The biotic soil CO_2 flux is largely controlled by processes including: (i) the respiration of soil micro-organisms (e.g. Lal and Bruce, 1999), and (ii) the respiration of plant roots (e.g. Bruggemann et al., 2011).

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The decomposition of soil OC by soil micro-organisms is controlled by: (i) the OC stock; (ii) the quality of the OC, defining the intrinsic decomposition rate; and (iii) series of environmental factors, e.g. temperature and access of microbes to water and oxygen (e.g. Bauer et al., 2012; Herbst et al., 2008). Environmental controls play key roles in OC dynamics and in the long term persistence of soil OC (Marschner et al., 2008; Kleber and Johnson, 2010; Schmidt et al., 2011; Dungait et al., 2012; Berhe and Kleber, 2013). Environmental controls reduce or amplify the intrinsic mineralization rate. OC decomposition can be mathematically described by equation 1.1 (e.g. Herbst et al., 2008):

$$\frac{dOC_i}{dt} = OC_i * (-K_{OCi}) * \prod fR_j \quad (\text{Eq. 1.1})$$

where OC_i is the amount of soil OC (kg.m^{-2}) stored in a pool i , K_{OCi} is the intrinsic mineralization rate of pool i , and $\prod fR_j$ a product of j reduction functions (dimensionless, ranging from 0 to 1) corresponding to the reduction/amplification effect of environmental conditions (e.g. temperature, access to water, to oxygen, and to micro-organisms, etc.) and to the reduction effect of spatial inaccessibility of OC for soil microorganisms (e.g. occlusion in soil aggregates).

Soil OC quality can then be defined as the ability of OC to supply organic molecules and to release carbon dioxide through metabolic pathways (i.e. soil micro-organisms respiration) (e.g. Kleber and Johnson, 2010; Dungait et al., 2012).

Behind the concept of OC quality, different kinds of physico-chemical stabilization mechanisms of OC exist. These operate at different timescales (von Lutzow et al., 2006). For instance, the OC stabilized by spatial inaccessibility (e.g. occlusion in soil aggregates) has been shown to decompose much faster (typical residence times of c. 1-100 years) than organic molecules stabilized by strong molecular interactions with mineral surfaces (typical residence times of c. 100-1000 years) (von Lutzow et al., 2006). Here, we

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consider that OC quality takes into account the effects of both the chemical and long-term stability of organic matter due to covalent linkages with soil reactive minerals (Krull et al. 2003; von Lützow et al., 2006; Kögel-Knabner et al., 2008b) as well as some physical protection mechanisms like soil micro-aggregates (e.g. Doetterl et al., 2012). However, short-term OC stabilization by spatial inaccessibility is not considered here in the concept of OC quality, but more as an additional reduction factor.

Soil micro-organisms need a source of thermal energy to allow enzymatic activities involved in their metabolic pathways (e.g. respiration). As a consequence, soil respiration exponentially increases with soil temperature (Howard and Howard, 1993; Fang and Moncrieff, 2001; Perrin et al., 2004). The sensitivity of soil OC to temperature is commonly expressed by the Q_{10} parameter (e.g. Conant et al., 2011). This reflects the increase in the flux rate due to a temperature increase of 10°C. The temperature sensitivity of soil OC decomposition (Q_{10}) is a key parameter when assessing the present and future behavior of the OC stocks under changing climatic conditions (Luan and Liu, 2012).

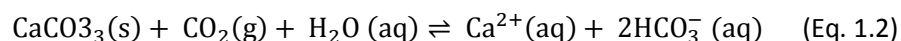
While a consensus has been reached about the exponential relation between soil respiration and soil temperature (Fang and Moncrieff, 2001; Perrin et al., 2004; Winkler et al., 1996), no global agreement exists about the relationship with soil moisture. Some authors suggest a bimodal relationship between soil water content and soil respiration: soil respiration firstly increases and then decreases (Bauer et al., 2012; Davidson et al., 1998; Perrin et al., 2004; Webster et al., 2008b). Others, such as in the conceptual background of the SOILCO2RothC model of soil OC dynamics (Herbst et al., 2008; Šimůnek and Suarez, 1993) consider a global positive impact of volumetric water content (VWC) on soil respiration (Akinremi et al., 1999; Castellano et al., 2011; Howard and Howard, 1993) as (i) soil water content increases the access of soil micro-organisms to their OC substrate, and (ii) soil micro-organisms need water for their own metabolic activities.

Recent studies (e.g. Ball, 2013) also showed that soil pore continuity and size are likely to determine greenhouse gases emissions. In other words, soil gas diffusion is impacted by both soil structural properties and soil VWC (Ball, 2013), as already accounted for in some OC dynamics models (Herbst et al., 2008; Šimůnek and Suarez, 1993). This may explain why the CO₂ efflux can sometimes deviate from the instantaneous soil respiration, due to CO₂ storage into soil pore spaces and later release (Ball, 2013; Maier et al., 2011). This CO₂ efflux not directly coming from soil respiration contributes to the so-called abiotic CO₂ flux.

1.1.3. Carbonates precipitation and abiotic CO₂ emission

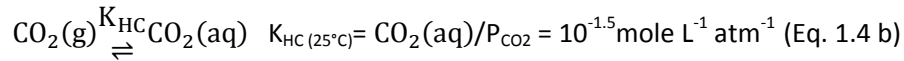
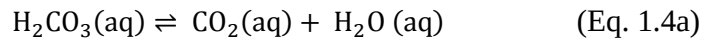
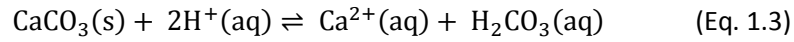
More recently, some studies have suggested that IC can also contribute substantially to the CO₂ fluxes between soil and atmosphere through abiotic processes (e.g. Emmerich, 2003; Inglis et al., 2009; Serrano-Ortiz et al., 2010).

In terms of C chemistry of the soil solution, some studies showed that, above a pH value of 6.3, abiotic CO₂ emission from soil is indeed associated to the reaction of soil carbonates precipitation (e.g. Gocke et al., 2010; Plummer et al., 1979; Serrano-Ortiz et al., 2010), as described in Eq. 1.2:



Soil carbonates dissolution leads to a net gaseous CO₂ consumption (Godd  ris et al., 2006 ; Lapenis et al., 2008) and to a CO₂ production in the liquid phase (i.e. H₂CO₃) (Serrano-Ortiz et al., 2010). In very acidic soils (when pH <5), the dissolution of soil carbonates acts as a net CO₂ source rather than a CO₂ sink (Plummer et al., 1979), as described in Eq. 1.3, where H₂CO₃ is in equilibrium with the gaseous form of CO₂ as described in Eq. 1.4 a-b (Appelo and Postma, 1994; Serrano-Ortiz et al., 2010):

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In dry conditions both under cold (e.g. Laponis et al., 2008) or hot climates (Dever et al., 1987; Emmerich, 2003; Kowalski et al., 2008; Serrano-Ortiz et al., 2010), abiotic CO_2 emissions have been observed. Depending on the studies, these are either suggested to contribute significantly to the total CO_2 flux (e.g. Laponis et al., 2008), or either not (e.g. Serrano-Ortiz et al., 2010).

While thermodynamic and kinetic controls of abiotic CO_2 fluxes from soil are well established (Appelo and Postma, 1994; Hamilton et al., 2007; Serrano-Ortiz et al., 2010), the quantification of abiotic CO_2 contribution to total CO_2 soil emissions remains challenging.

1.2. The role of soil C in ecosystem functions and services

1.2.1. Soil C and the climate change issue

The C cycle on earth is a function of four main reservoirs in interaction with each other (e.g. Eswaran et al., 1993; Grace, 2004), as illustrated on Figure 1.1. These reservoirs are the oceans (38 000 Pg C), the atmosphere (750 Pg C), the terrestrial systems (2050 Pg C) and the part of the geological systems forming the fossil fuels (4 000 Pg C). The terrestrial reservoir is composed of two different pools: the vegetation biomass (550 Pg C) and the soil C (1500 to 2200 Pg C in the first soil meter) (e.g. Eswaran et al., 1993; Batjes, 2014). More precisely, soils contain c. 1500 Pg C in the form of organic matter and c. 700 Pg C in the form of inorganic matter in the top first soil meter (Batjes, 2014). The world pool of soil organic carbon (OC) exceeds c. 2500 Pg C if deeper soil layers

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are accounted for (Batjes, 2014). Hence, by storing C in soil organic matter (e.g. Lal and Bruce 1999; Batjes, 2014) and soil carbonates (e.g. Batjes, 2014; Schlesinger et al., 1985; 2009), soils play an important role in the C cycle, and constitute an important part of the global C pool. Soils are estimated to contain c. 2 to 3 times more C than the atmosphere and c. 3 times more C than the aboveground biotic/vegetational pool (Eswaran et al., 1993; Grace, 2004).

In addition to its ability to store important amounts of C, the soil system can potentially play a major role in atmospheric C emissions (Eswaran et al., 1993; Lal et al., 2003; Schimel et al., 2001; Kuzyakov, 2006). The flux of C from soils mainly occurs in the form of CO₂, as a result of heterotrophic respiration (i.e. from soil micro-organisms) and autotrophic respiration (i.e. from plant roots) (e.g. Lal and Bruce, 1999; Rustad et al., 2000) as explained in section 1.1.2. This annual CO₂ flux from soils is estimated to average c. 68 to c. 100 Pg C yr⁻¹ (depending on the studies) at a global scale, based on extrapolations from biome land areas (Musselman and Fox, 1991; Raich and Schlesinger, 1992; Raich and Potter, 1995; Rustad et al., 2000). In comparison, only c. 9 Pg C yr⁻¹ is lost to the atmosphere due to fossil fuel combustion, and only c. 1.6 Pg C yr⁻¹ is emitted to the atmosphere as a consequence of land use changes mainly through deforestation in tropical regions (Grace, 2004; Lal 2003; Schimel et al., 2001). Hence, CO₂ fluxes from soils constitute the first largest positive C flux to the atmosphere. Of course, the CO₂ flux from soil is balanced by photosynthesis (Kuzyakov, 2006), characterized by a gross primary productivity estimated to range between 100 and 120 Pg C yr⁻¹ (e.g. Rustad et al., 2000; Schlesinger and Andrews, 2000). Considering also plant respiration, this results in a net terrestrial uptake of c. 1.4 Pg C yr⁻¹ (Lal 2003; Schimel et al., 2001). The atmospheric sources mentioned above are also balanced by an accumulation in the atmosphere (c. 3.2 Pg C yr⁻¹) and by the oceans uptake (c. 1.7 Pg C yr⁻¹) (Lal 2003; Schimel et al., 2001). In order to balance the global C budget (Figure 1.1), researchers pointed out a residual “missing sink” of 2 to 4 Pg C yr⁻¹ (Houghton, 2007; Lal 2003; Schimel et al., 2001).

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Given the small difference between the estimated positive and negative terrestrial C fluxes (i.e. the soil respiration and the gross primary productivity through photosynthesis, respectively), even a small change in soil respiration or in its estimation could increase or decrease the strength of the terrestrial C sink or transform it into a global C source (Rustad et al., 2000). Yet, current predictions of the exchange of C between the soil and the atmosphere are associated with large uncertainties (Houghton et al., 2003; Peters et al., 2010). In addition, a positive feedback to climate change could occur in the coming period if the climate warming would induce an acceleration of soil OC decomposition (Davidson and Janssens, 2006). Hence, a thorough quantification and a better understanding of the soil-atmosphere C exchanges is of high importance to adopt strategies to mitigate climate change.

As summarized by scientific experts of the Intergovernmental Panel on Climate Change (IPCC), CO₂ plays a key role in global change processes on earth and is of considerable concern in global climate change because of its greenhouse gas warming potential (IPCC, 1990, 1992). Greenhouse gases like CO₂ affect climate by altering incoming solar radiation and outgoing infrared (thermal) radiation that are part of Earth's energy balance. Changing the atmospheric abundance or properties of these gases and particles can lead to a warming or cooling of the climate system (IPCC, 2007b).

Recent studies (e.g. Hofmann et al., 2009) demonstrated that the concentration of CO₂ in the atmosphere is increasing since the beginning of the industrial revolution (c. year 1800), as illustrated on Figure 1.2 for the past 50 years. The atmospheric concentration of CO₂ has increased globally by about 100 ppm (36%) over the last 250 years, from a range of 275 to 285 ppm in the pre-industrial era (AD 1000–1750) to 379 ppm in 2005 (IPCC, 2007a).

The Global Carbon Cycle, Biotic

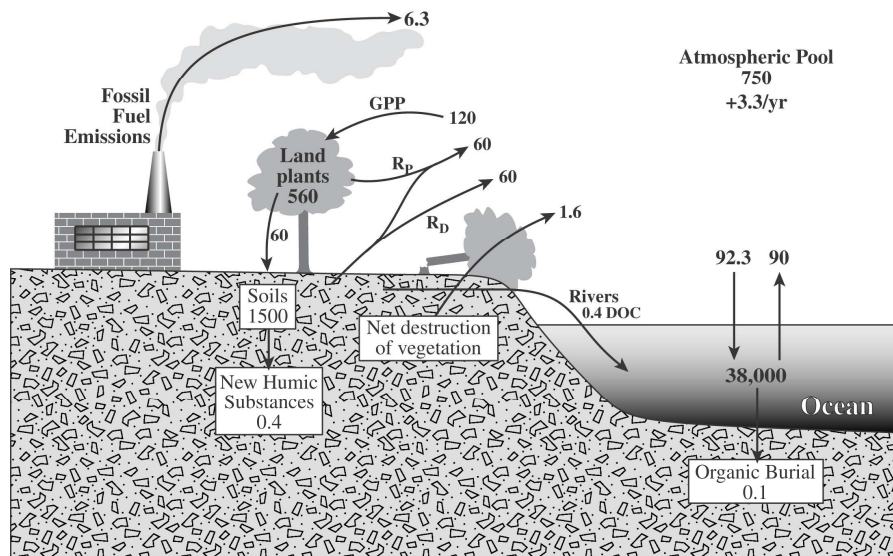


Figure 1.1. The global carbon cycle. All pools are expressed in units of Gt C and all fluxes in units of Gt C/yr, averaged for the 1980s. GPP= Gross Primary Productivity, R_p = autotrophic respiration, R_D = heterotrophic respiration. Source: Schlesinger and Andrews (2000).

According to the IPCC, the increases in global atmospheric CO_2 since the industrial revolution seem to be mainly due to CO_2 emissions from the combustion of fossil fuels, the gas flaring, the cement production, and the land use changes (IPCC, 2007a). Hence, human activities contribute to climate change mainly by causing changes in Earth's atmosphere in the amounts of greenhouse gases like CO_2 (IPCC, 2007a). The human impact on climate during this era greatly exceeds changes due to natural processes, such as solar changes and volcanic eruptions (IPCC, 2007a, 2007b). The anthropogenic component of the atmospheric CO_2 concentration (atmospheric value reduced by the pre-industrial value of 280 ppm) follows an exponential increase with a doubling time of c. 30 years (Hofmann et al., 2009).

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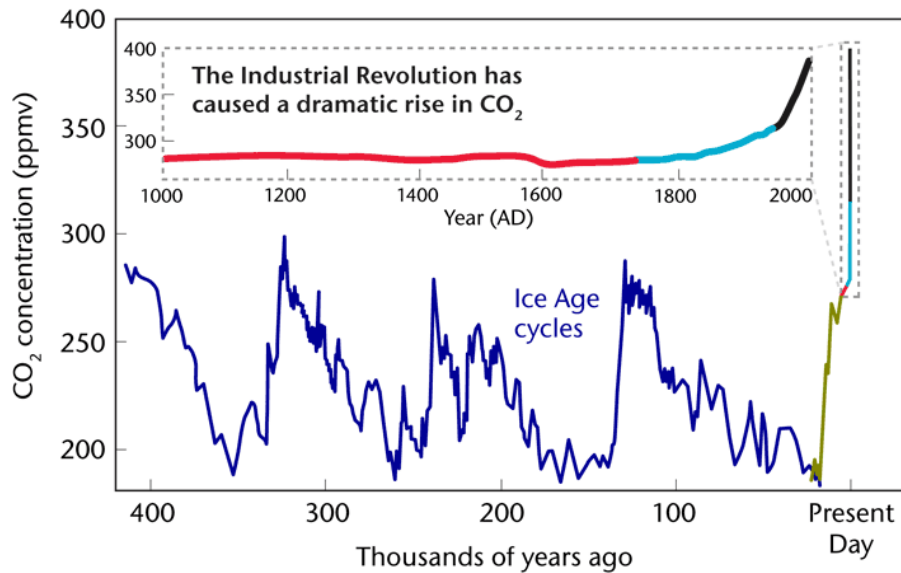


Figure 1.2. Time evolution across geological ages of atmospheric carbon dioxide concentration (measured from ice cores). (Sources: Hofmann et al., 2009; MET office, 2014)

Since the start of the industrial era, the overall effect of human activities on climate has been a warming influence (IPCC, 2007a; 2007b). Many authors demonstrated several current and future impacts of climate change on human well-being and ecological issues, i.e. impacting the freshwater resources (Kundzewicz, 2008), the agriculture and food security (e.g. Blanc and Reilly, 2013), living systems (e.g. Parmesan and Yohe, 2003), and human health (Patz et al., 2005).

1.2.2. Soil OC depletion

Soil organic carbon is the most important indicator of soil quality and agronomic sustainability because of its impact on other physical, chemical and biological indicators of soil quality (Reeves, 1997). As a soil colloid, organic matter interacts with organic and mineral substances (e.g. Schnitzer, 1991). This property of soil OM has several important impacts on ecosystemic

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services. First, soil OM retains soil nutrients and facilitates the transformation of organic substances into available substances by plants roots, which make them an important control of crop yield (e.g. Reeves, 1997). Second, soil OM also plays an important role in reducing the leaching of pollutants (e.g. pesticides) in groundwater (e.g. Leterme et al., 2007 ; Heuvelink et al., 2010), and is a key factor in the preservation of the quality of drinkable groundwater. Third, the organic binding agents (present in some soil OM molecules or produced by micro-organisms feeding with soil OM) link with clays minerals to form soil aggregates, improving the soil structure (e.g. Tisdall and Oades, 2006). A good soil structure allows a better infiltration of rain water, which e.g. improves crop yields and allows to avoid floods and mudslides (e.g. Porazinska and Wall, 2001). Last but not least, soil OM constitutes an important reservoir of C on earth (e.g. Batjes, 2014; Eswaran et al., 1993; Grace, 2004), as further explained in section 1.2.1 .

At a global scale, studies have shown that deforestation and more widely land use change (Fig. 1.3) can result in 20 to 50% loss of the C stored in soils, largely through erosion (Eswaran et al., 1993; Batjes, 2014; Guo and Gifford, 2002; Lal et al., 2003; Schimel et al., 2001). At a regional scale, it was also demonstrated that land use and management impacts accounted for more than 70% of the variation in observed soil OC changes (van Wesemael et al., 2010). Swift (2001) showed that grassland soils converted to cropland lose 20-50% of their OC in 40 to 50 years. The cultivation of grassland and forest soils in Canada also resulted in important losses of soil OC (Janzen et al., 1998). Under cropland, Goidts and van Wesemael (2007) highlighted that in a 50 years period (from 1955 to 2005) of monitoring on the agricultural soils of southern Belgium (Wallonia), an average decrease of 5.8 Mg C ha^{-1} was measured in the plough layer (0-30cm depth) from an initial equivalent soil OC stock of $46.4 \text{ Mg C ha}^{-1}$.

This depletion is due to both human driving forces (land management) and inherent soil properties i.e. texture and drainage (Goidts and van Wesemael, 2007; Guo and Gifford, 2002; Meersmans et al., 2011). Croplands in the loam region of Wallonia have reached soil OC concentrations close to

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10 g C kg⁻¹ indicating that these soils are at risk of a decline in aggregate stability (e.g. Golchin et al., 1994; Meersmans et al., 2011). Further research is needed to gain more insight into the processes driving the observed soil OC trends (Meersmans et al., 2011). For now, this decrease in soil OC stocks observed for cropland has been explained by the decrease in mass of farmyard manure and slurry applied on cropland along with the change in the types of crops cultivated (progressive replacement of cereals by root crops and fodder) (Goidts and van Wesemael, 2007; Goidts et al., 2009; West and Post, 2002), as well as by conventional tillage practices (West and Post, 2002).

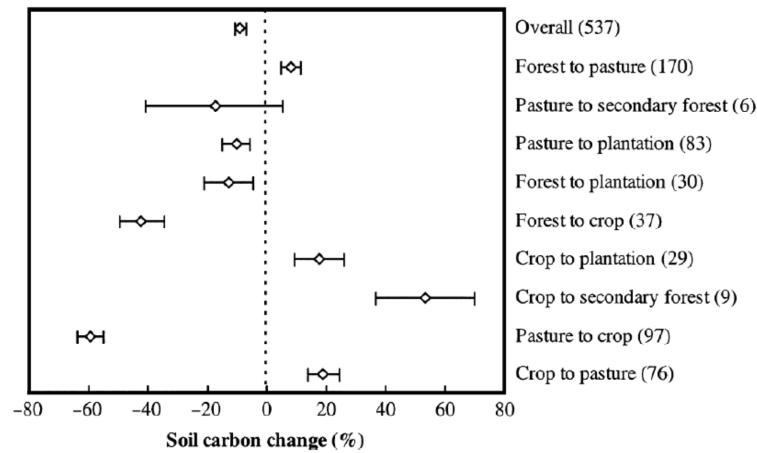


Figure 1.3. Soil carbon response to various land use changes (95% confidence intervals are shown and numbers of observations are in parenthesis). (Source: Guo and Gifford, 2002).

1.3. The hillslope as elementary unit for studying soil C dynamic processes

Soil erosion-induced C loss is a severe global problem, especially in agricultural ecosystems in sloping regions (Lal 2003, Reicosky et al. 2005). However, although transfer of soil OC by erosion has been recognized, and that a strong linkage between soil OC dynamics and landscape processes has been illustrated

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by Stallard (1998), its impact on both local and global C budgets is poorly understood (Lal 2003; Van Oost et al. 2007, 2012).

Contradictory conclusions about the influence of soil erosion on C cycles are observed (Manies et al. 2001, Van Oost et al. 2007). Most studies suggest that terrestrial sedimentary processes constitute a net C sink: sedimentation in low mineralization contexts, and not erosion-induced oxidation, will dominate the C budget (e.g. Stallard 1998, Harden et al. 1999, Smith et al. 2001, Smith et al. 2005, Van Oost et al. 2007, 2012). Van Oost et al. (2005a; 2007) suggested a negative terrestrial C flux (i.e. a net C sequestration in soils) of c. $0.12 \text{ Pg C yr}^{-1}$ at the global scale. In contrast, other studies suggested a positive flux from terrestrial ecosystems to the atmosphere ranging from $0.37 \text{ Pg C yr}^{-1}$ (Jacinthe and Lal 2001) to $0.8\text{-}1.2 \text{ Pg C yr}^{-1}$ (Lal 2003). More recently, Van Oost et al. (2012) highlighted that the dynamic phase of buried C in terrestrial depositional stocks (Fig. 1.4.) may substantially limit the erosion-induced C sink strength at centennial timescales. In addition to potential increases in decomposition rates of buried C as a result of global warming, desiccation of saturated soils, land use change, and re-excavation by gullying, the time lag in buried C losses implies that this large store of recently buried C cannot be assumed to be inert to further loss, and indeed might become a significant C source (Van Oost et al., 2012).

At the scale of landscapes, soil OC transfers occurring from the top to the bottom of the slopes, combined with gradients in environmental factors like soil water content along the slope, may affect the spatial distribution of both the quantity and the quality of soil OC, especially on agricultural land (Berhe et al., 2012; Doetterl et al., 2012; Nadeau et al., 2012; Jacinthe and Lal 2001, Van Oost et al. 2005a). During erosion and lateral transfer of sediments, the fate of soil OC is subject to many uncertainties.

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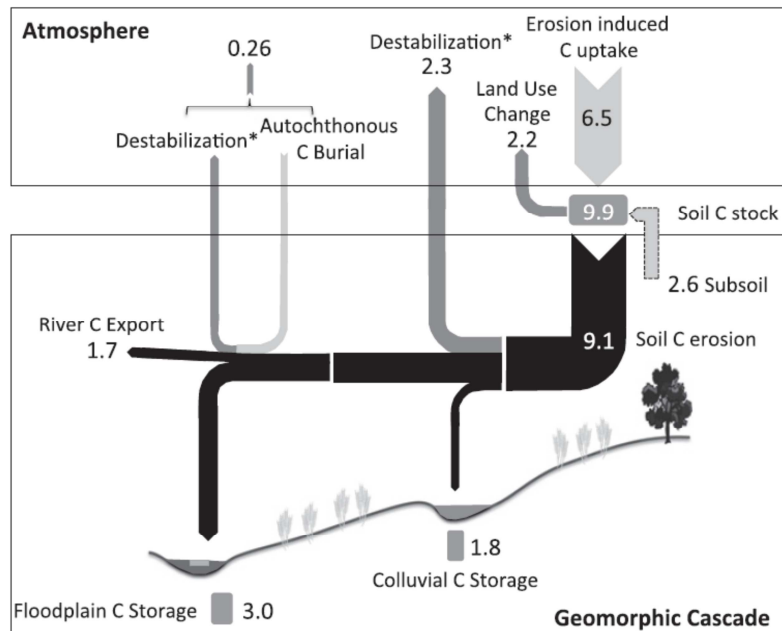


Figure 1.4. Net exchange of C (in Tg C) between the soil and atmosphere as a result of accelerated erosion integrated for the period 4000 B.C. to A.D. 2000 for the Dijle catchment. Boxes represent reservoirs, black arrows represent lateral C fluxes, dark gray arrows represent mineralization of buried C in depositional environments, and light gray arrows represent soil C inputs. The land use change flux is the direct (non-erosion-related) effect of ALCC on soil C storage. The soil thus is both a source and a sink, where the sink term is greater than the source term. The soil C stock is the estimated initial C stock for the upper 1 m of the profile before the start of agriculture (4000 B.C.). *The possible mechanisms leading to destabilization of buried C are decomposition, i.e., a CO₂ flux toward the atmosphere, and leaching losses. (Source: Van Oost et al., 2012)

Three key geomorphological mechanisms, acting together or separately, have been identified to describe the OC dynamics at the hillslope scale (Stallard 1998, Van Oost et al. 2007). First, an increase in the oxidation rate of soil OC during its translocation may entail a net erosion-induced C loss. This enhanced decomposition of soil OC as a result of the chemical and physical breakdown of soil particles (e.g. aggregates disruption) during detachment and transport. Second, soil OC may be replaced at eroding sites, resulting of continued inputs

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from plant materials, which could mitigate this C loss. Third, once brought at the bottom of the slope, sediments deposits enriched in soil OC accumulate and are progressively buried deeper and deeper along the soil profiles. This third mechanism results in the development of colluvium at the depositional site with an increasing soil OC stock (Lal 2003, Van Oost et al. 2005a, Van Oost et al. 2005b). Finally, eroded C may also be delivered to the fluvial system and the global ocean (Battin et al., 2008; Richey et al., 2002). However, no consensus neither clear conceptual model exists about the fate of deeply buried OC at depositional sites in upland areas. Indeed, a series of complex and interacting processes are involved in burial sites, and the processes that reduce or enhance mineralization in these conditions is still poorly documented (Lal 2003; Van Oost et al. 2005a, 2005b, 2007; 2012).

On one hand, some modeling experiments suggest that net C sequestration occurs at the depositional sites (e.g. Smith et al. 2005), while others negate the apparent C sink caused by soil OC burial at depositional sites (e.g. Yoo et al. 2005). Field measurements have shown that very high amount of soil OC can be stored in the subsoil until 1-2 or even 3 m depth (Jobbagy and Jackson, 2000; Don et al., 2007), especially in colluvium (e.g. Magdoff 2004). Some studies have even shown an increasing soil OC stabilization with depth along soil profiles (Lorenz and Lal, 2005).

On the other hand, Rumpel and Kögel-Knabner (2011) highlighted that deep soil OC is highly processed, indicating their potential role in soil C dynamics and surface CO₂ fluxes. Under some dry specific climatic conditions, field measurements have shown this deep carbon stock to contribute substantially to total soil respiration (Carlisle et al. 2006, Gillabel 2010). Recently, some studies reported higher respiration rates (used as indicator of soil OC persistence, e.g. Gregorich et al., 1994) at footslope positions, relative to summit and shoulder positions (Reicosky et al., 2005; Webster et al., 2008b), while opposite trends were also reported in Epron et al. (2006) and Wang et al. (2013). Other studies did not detect differences in soil surface CO₂ respiration along hillslopes (e.g. Fiener et al., 2012).

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Hence, it is of high importance to evaluate more precisely if depositional areas, and to a larger extent entire hillslopes, have to be considered as erosion-induced C sinks or erosion-induced C sources. In order to take into account the erosion impact on the global carbon budget, it is important to better understand the link between soil OC dynamics and landscape processes, and to establish C budgets at the hillslope scale taking into account all the relevant mechanistic processes and factors causing C losses or C sequestrations at the catchment scale (Stallard 1998). Recently, researchers have highlighted the need to consider soils as mobile systems (Quinton et al., 2010). However, current approaches for quantifying OC turnover in soils are typically informed by 1-D vertical modelling concepts that focus on the understanding of soil OC turnover in flat, non-sloping landscapes.

In summary, the potential significant role of landscape-scale processes (mainly lateral fluxes of sediment, C and water) and subsoil processes for the C cycle has been highlighted by many studies during the last 10 years. However, until now most studies are observational and report on empirical relations describing the spatial and temporal variability of C stocks, and to a lesser extent C stability, in relation to geomorphic processes. As a result, a detailed mechanistic understanding of the processes regulating soil CO₂ respiration at the scale of hillslope is far from complete.

Based on the state-of-the-art described above, we identified the following key research questions:

- What are the main processes and controls on the spatial distribution and on the persistence of soil OC along a hillslope?
- Does soil IC contribute to CO₂ fluxes, and to what extent?
- What is the contribution to surface CO₂ fluxes of buried soil OC at depositional sites?
- How important are the soil-atmosphere CO₂ emissions at the summit, at the depositional downslope position, and at the entire hillslope scale?

1.4. Thesis objectives and layout

The overall objective of the presented thesis is to improve our mechanistic understanding of soil organic carbon dynamics at the hillslope scale by quantifying and modelling CO₂ fluxes to the atmosphere and their controlling factors under the pedo-climatic context of the Belgian loess belt. As such, this thesis aims to advance the science by (i) improving our understanding of the processes that control OC persistence in eroding landscapes and (ii) quantifying spatial and temporal patterns of soil-CO₂ emissions at the hillslope scale.

To implement these objectives, we structured the thesis into 8 chapters. Main contents of the thesis are detailed in chapters 3 to 7. Linkages between these chapters are illustrated by on Figure 1.5.

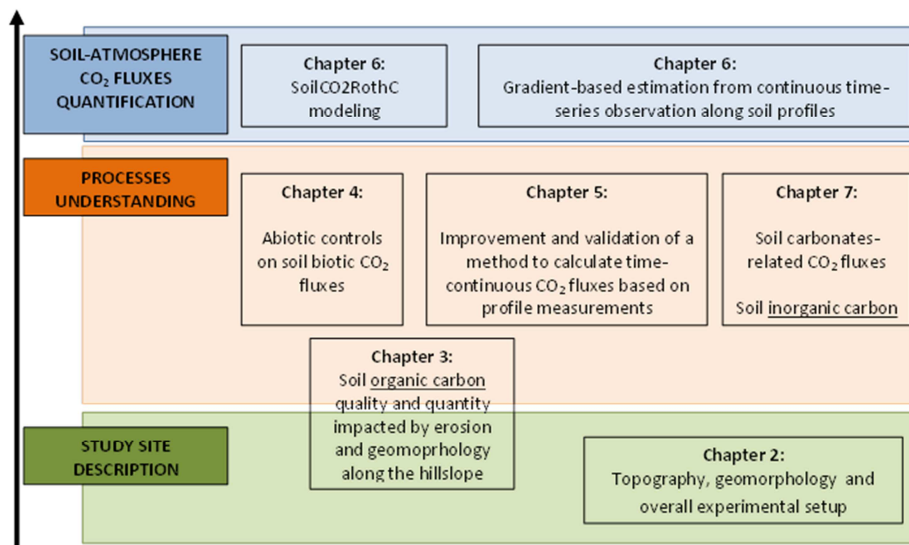


Figure 1.5. Schematic overview of the thesis outline (the black arrow represents the logical succession and the links between chapters).

In chapter 2, we briefly describe the pedo-climatic context of the study site, as well as its geomorphological characteristics. We explain the toposequence

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approach whereby measurement stations were selected at different slope positions along a transect. This chapter also gives an overview of the experimental setup.

In chapter 3, we provide a quantitative description of the OC pools along the hillslope, and secondly provide important information about the mechanisms governing the distribution of soil OC quality along an eroding hillslope on loess soil. This is based on three types of laboratory experiments. First, we assess cumulative soil erosion using diagnostic soil horizons and the ^{137}Cs techniques. Second, we determine organic carbon (OC) stocks and its quality using NaOCl oxidation method. Third, we characterize reactive soil mineral phases.

In chapter 4, we study the apparent persistence of soil OC along the hillslope using in situ soil surface heterotrophic respiration measurements as an indicator. Here, we use a regression model to elucidate and quantify the role of abiotic factors controlling soil organic carbon persistence along the hillslope, i.e. soil moisture, soil temperature, soil OC quantity and quality. We also quantify and describe the spatial distribution of CO_2 fluxes.

In chapter 5, we provide new insights to improve the gradient-based method for assessing CO_2 fluxes in loamy soils, based on CO_2 concentration profiles measured by means of the non-dispersive infra-red (NDIR) technology. In particular, we evaluate the different calculation methods to assess CO_2 diffusivity. The gradient based method uses water content and CO_2 concentration collected in situ along soil profiles. The surface CO_2 fluxes measurements presented in chapter 4 are used here for the validation of different calculation methods.

In chapter 6, using continuous times-series of soil CO_2 concentration, soil VWC and soil temperature at different depths along two soil profiles (i.e. the summit and the footslope), we compute a continuous times-series of soil CO_2 fluxes at the surface and along the soil profile, enabling a vertical partitioning of soil CO_2 fluxes. Using the 1-D OC dynamic SOILCO₂-RothC model, calibrated with in-situ measurements and benefiting from the conceptual improvements described in

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the previous chapters, we quantified the soil-atmosphere C flux both at summit and downslope positions. Finally, we upscaled these results at the hillslope scale.

In chapter 7, the state-of-art of physico-chemical processes governing carbonates-related soil CO₂ fluxes is reviewed. Based on this, we elaborate on the appropriateness to consider carbonates related to soil CO₂ fluxes in temperate climatic conditions. Field measurements of atmospheric C emission achieved in chapter 4 and 6 are re-employed here to elucidate the role of carbonates in soil C emissions.

Chapter 8 summarizes the main findings and take-home messages, presents the limitations and perspectives for future researches, and formulates a general conclusion.

Chapter 1

2. Study site description

2.1. Geographic and climatic context

2.1.1. Catchment location and features

The southern part of Belgium (Wallonia) displays a wide diversity of soils and land uses. Their combination leads to 10 categories of agro-ecological regions (Figure 2.1.). This study was carried out in Louvain-la-Neuve, in the sandy-loam area of the Belgian loess belt, in the northern part of Wallonia (Figure 2.1.). The meteorological data used in this study were collected in Louvain-la-Neuve, by means of a meteo station of the Pameseb Network (Figure 2.1.), situated at c. 2 km from the study site.

Experiments were conducted along a 150 meters hillslope situated on a cropland (50.6669°N, 4.6331° W) (Figure 2.2.). We used a toposequence approach whereby 5 measurement stations were selected at different slope positions along a transect: the summit, the convex shoulder, the backslope, the toeslope and the footslope (Figure 2.2 and 2.4). We selected these 5 slope positions in order to maximize differences in erosion and deposition rates. The slope percentage in the backslope area ranges between 8.5 and 16%, with a mean slope of 12%. The slope percentage in the convex shoulder area ranges between 4 to 8.5%, with an average of 6%. The difference of elevation between the summit and the footslope is c. 10 meters (Figure 2.4).

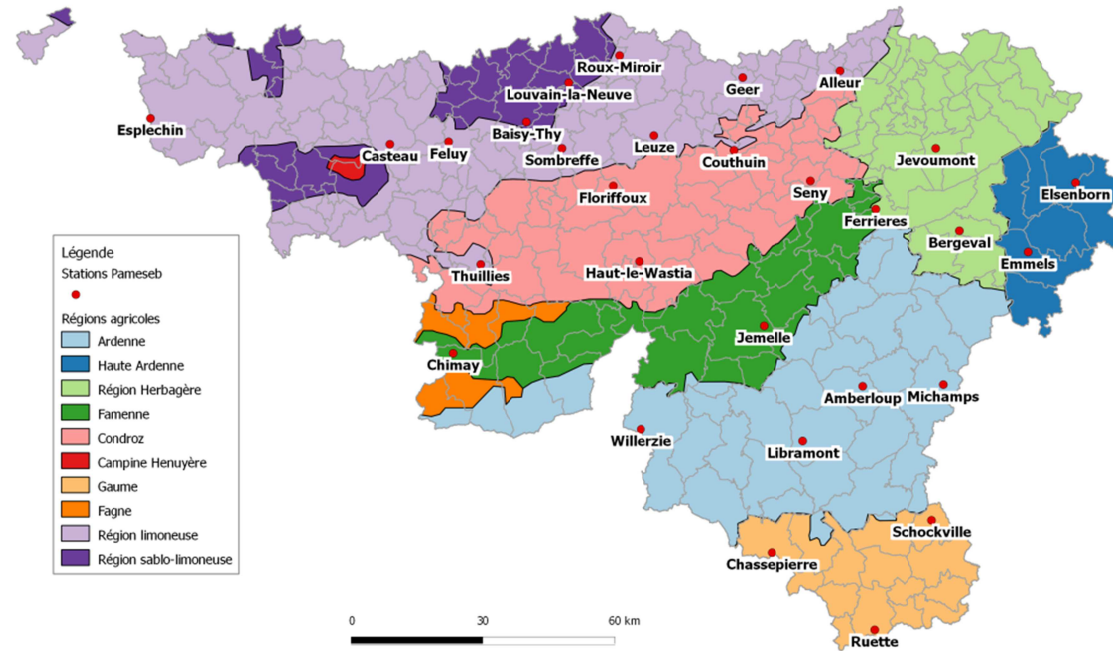


Figure 2.1. Agro-ecological regions (colored areas) and meteorological stations (red points) in Wallonia (Southern Belgium). (Source: Pameseb, 2014)



Figure 2.2. Plan view of the study site (both the cropland and the reference uneroded summit on grassland) showing the persistence along time of its land use: (a) in 1955, (b) in 1963, (c) in 1981, and (d) in 2013. Outlines of the studied cropland, transect and measurements stations are drawn on figure d; adapted from Google Maps©.. Figures a, b and c were adapted from Institut Géographique National, Belgium.

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The transect was oriented parallel to the direction of tillage (Figure 2.2) and shows little slope convergence/divergence. Given that the other contributing slope is characterized by a very different soil texture (sand), we were able to identify the boundary in the depositional area between the two hillslopes and select a footslope where we could exclude lateral soil translocation from other hillslopes.

The field is plowed (0-30 cm soil surface layer) every year. Manure and nitrate application are also carried out, each four years and each year, respectively. The current crop rotation is winter wheat, maize and spring wheat. In order to ensure that the processes occurring on the study site have reached a dynamic equilibrium, and that no external perturbation could have introduced bias in the observations in terms of soil pedogenesis, geomorphology, and OC dynamics, a simple historical research about its land use was carried out (Figure 2.2). Agriculture in the region started in the Bronze/Iron age. We have no information on the long-term agricultural history of our study site but it has been under continuous agricultural land use since at least 1770 (Lannoo, 2009). Four aerial pictures or land use maps from year 1955 to the end of the study (2013) demonstrate the persistence along time for the c. 60 last years of the land use of our study site as a cropland, as well as of the nearby grassland used as a reference summit preserved from erosion (Figure 2.2).

2.1.2. Climatic characteristics

The climate of the study site is maritime temperate, with an average annual temperature of 9.7°C and an average annual precipitation of 805 mm. Time-series of the daily precipitation and evapotranspiration were calculated for each year from 2011 to 2013 (Figure 2.3.). Evapotranspiration was calculated based on meteorological records (section 2.1.1.) according to Penman-Monteith equation (FAO, 2014). The temporal dynamic and overall importance of both temperature and water supply are different for the three studied years (Figure 2.3.). The year 2013 was globally dryer than 2011 and 2012. Spring 2011 (days of year 50 to 150) was especially dry. The higher peaks of precipitation

Study site description

(i.e. exceeding 40 mm d^{-1}) were observed in 2012, both in spring and in autumn. Mean daily temperatures ranged from -2°C to 25°C in 2011, -10°C to 28°C in 2012, and -5°C to 28°C in 2013. Temperature was globally higher and less dynamic in time in 2011, while more seasonal contrasts were observed in 2012 and 2013 (Figure 2.3.).

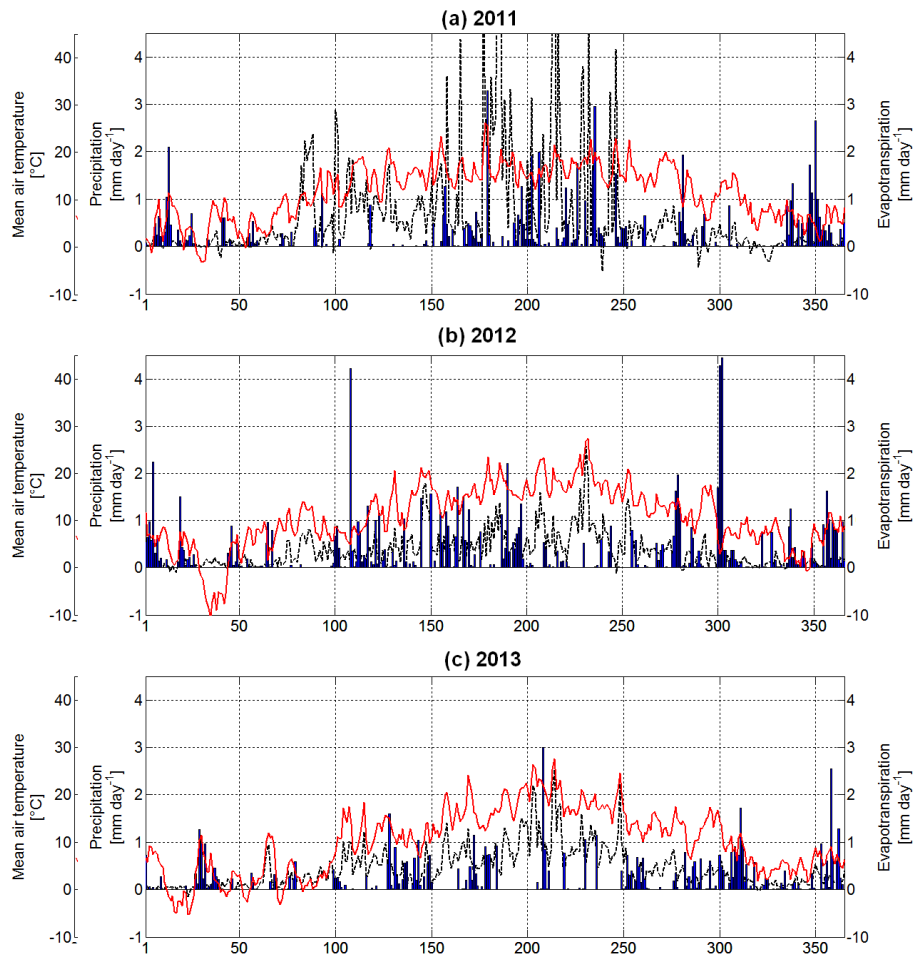


Figure 2.3. Time-series of the daily precipitation (blue bars) and evapotranspiration (slashed blacks lines) and temperature (red plain lines) at the study site in: (a) 2011; (b) 2012; (c) 2013.

2.2. Geomorphic and pedological context

2.2.1. The loess belt

The current geological period, i.e. the Quaternary area, which began c. $2.6 \cdot 10^6$ years BP, is characterized by glacial periods in its first phase (i.e. the Pleistocene area). During these glaciations, the glaciers eroded and carried important amounts of calcareous rocks. In Europe, the last of these glacial periods is called the Weichsel age, and was particularly hard, leading to the formation of cold desert conditions (Boulvain and Pingot, 2014). These glaciations also induced a decrease of the sea level and an important withdrawal of water from the European continent, especially important during the Weichsel age (Fig. 2.4).

Hence, alluvial carbonated deposits (mainly coming from the Scandinavian Glaciers as far as the Weichsel age is concerned) emerged at the current location of the Northern sea (Boulvain and Pingot, 2014). This alluvial carbonated dust was taken and transported by a strong wind coming from the North, through the processes of deflation and suspension, respectively (Boulvain and Pingot, 2014). According to the physical Stokes' law, these eolian particles were then deposited at the soil surface, at a distance inversely proportional to their mass and their textural class: first sand (from 50 μm to 2 mm), then silt (from 50 to 2 μm), and further clay particles ($<2 \mu\text{m}$). The thickness of this loess mantle ranged from 10 to 20 meters (Boulvain and Pingot, 2014). This unweathered loess initially contained 10-13% CaCO_3 . The silt deposits formed the current Loess belt (Fig. 2.4).

This loess belt can be observed in middle Belgium, and is called Brabantian Loess (Boulvain and Pingot, 2014). The loess was mainly deposited on hillslopes exposed to the Northern winds, and was afterwards especially preserved inside depressions of hilly reliefs. This explains why one cannot observe loess deposits on some hillslopes oriented to the South. This is the case of the hillslope situated in front of the hillslope studied in this thesis (Figure 2.6).

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After the Weichsel age, at 10 000 years BP, a global climate warming occurred, and a warm interglacial period began, the Holocene (i.e. the second and current period of the Quaternary area). Along the Holocene, the Brabantian Loess progressively decalcified at the soil surface and got enriched in clay (up to 30%) through pedogenesis (Boulvain and Pingot, 2014), leading to the formation of the current Belgian loamy agro-ecological region (Fig. 2.1). This pedogenesis is assumed to have resulted in a spatially uniform decalcification of the loess in the landscape (Brahya et al., 2000; Rommens et al., 2005). In our regions, a reference of 230 ($\pm$ 12) cm has been used for the depth of the decarbonated loess (Brahya et al., 2000; Rommens et al., 2005).

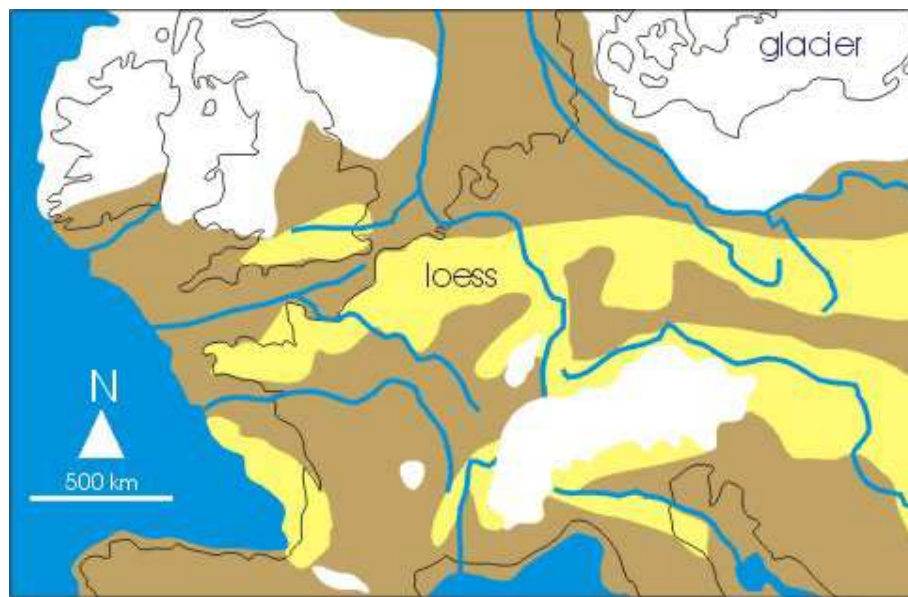


Figure 2.4. Extent of the Loess deposits from the last glaciation period of the Quaternary area (Weichsel age, Europe): Loess in yellow, other emerged surfaces in brown, glaciers in white, sea and rivers in blue. (Source: Boulvain and Pingot, 2014)

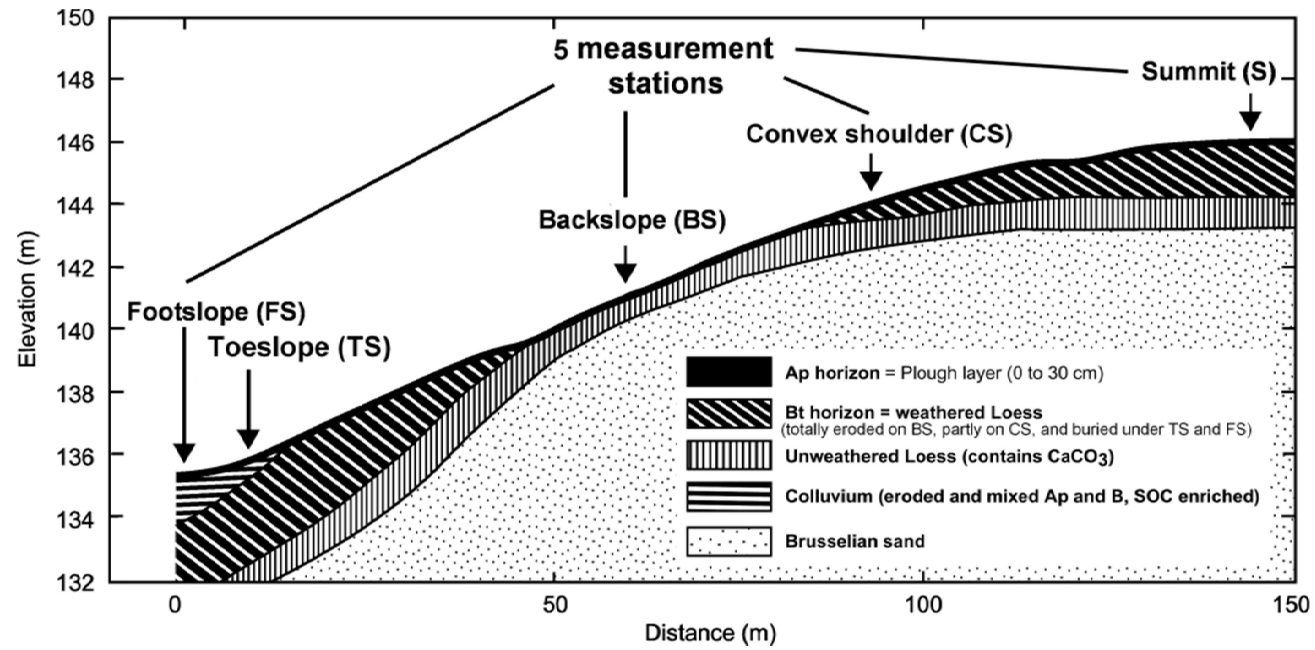


Figure 2.5. Schematic profile view of the hillslope and its geomorphology. Oriented Est-West (from left to right).

Study site description

Hence, the soil parental material along the hillslope studied in this thesis consists of loess of Weichsel age (about 20 000 BP), and is underlain by tertiary Brusselian sands (Fig. 2.5). This hillslope was likely exposed to intensive soil erosion, leading to a transfer of soil material from the summit and the slope to the footslope (Fig. 2.5). At the backslope position, an important amount of soil was removed and the calcareous parent material is surfacing. The convex shoulder position is characterized by a soil truncation, but still displays weathered decarbonated loess at the soil surface. Downslope, sediment deposits have accumulated, and were buried deeper and deeper along the successive erosion events, forming a so-called colluvium, enriched in soil OM (Fig. 2.5). The median age of colluvial deposits in the region is c. 600 years (Notebaert et al 2011).

2.2.2. The resulting soils gradient

According to the numerical soil map of Wallonia (DGARNE, 2010), to a more detailed textural analyses performed by an independent soil laboratory (CPBW, 2011), and to the World Reference Base for Soil Resources (WRB, 2014), a pedological gradient develops along the studied transect. A detailed soil analytical board is presented in the results section of chapter 3 (Table 3.1).

All along the hillslope, soil texture is classified as loam or silt-loam (letter A, Figure 2.6), with a favorable drainage class (letter b, Figure 2.6). This means that the natural drainage of water through the soil profiles is theoretically very good, and long periods of water saturation should not occur, preventing soil from anoxic conditions and from oxydo-reduction reactions (Légende de la Carte Numérique des Sols de Wallonie, FUSAGx, 2005).

The soils along the studied gradient differ in their profile development (third letter in the Belgian classification code, Figure 2.6). The toposequence consists of a Dystric Luvisol at the summit and the convex shoulder, an Eutric Cambisol at the backslope position, while a Colluvic Regosol is observed in the

depositional area at the footslope (WRB, 2014), as illustrated on Figures 2.5 and 2.6.

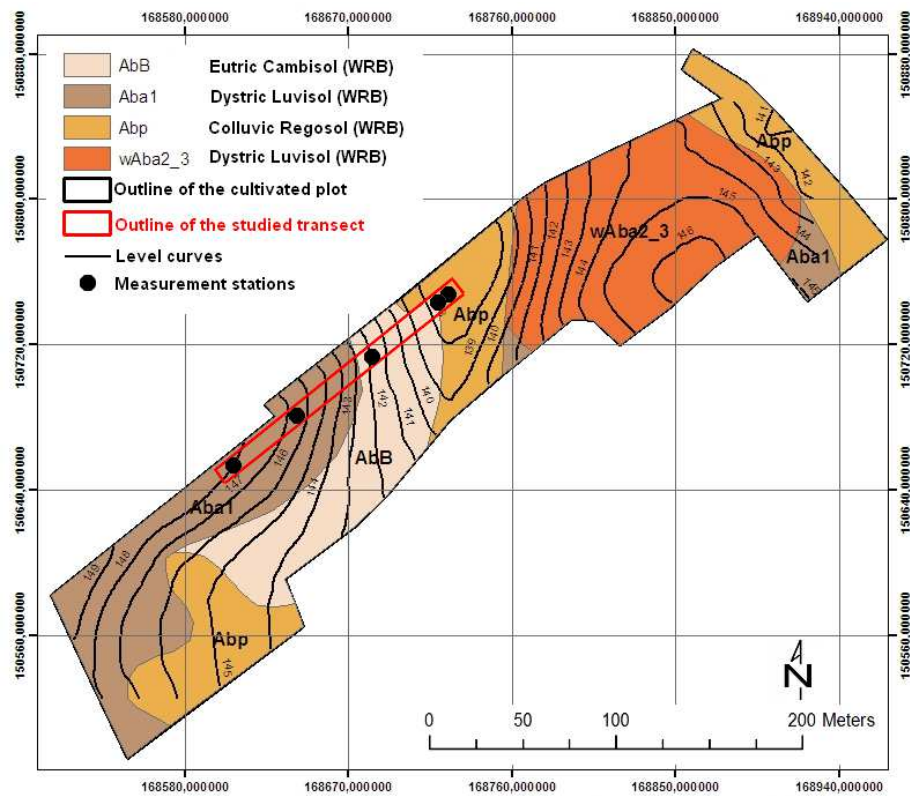


Figure 2.6. Map of the study site, its topography and its pedological features (the soil map was build with data from the Carte Numérique des Sols de Wallonie, DGARNE, 2010). Oriented West-Est (from left to right).

Study site description

A Dystric Luvisol (Figure 2.7. a), as encountered both at the summit and at the convex shoulder positions (Figures 2.5 and 2.6), is a soil formed on silty aeolian deposits characterized by the migration of secondary clays minerals from the top soil due to soil weathering, forming an argic textural B horizon (Bt, as indicated by the Aba Belgian classification on Figure 2.6). This Bt horizon contains high activity clays and is characterized by a base saturation < 50%, these two criterions justifying the Dystric qualifier (WRB, 2014). The base saturation becomes higher in the underlying unweathered and carbonated C horizon (Figure 2.7. a). At the topsoil (between the soil surface and the argic horizon), the loss of iron oxides together with clay minerals may lead to a bleached eluviation (E) horizon (WRB, 2014). However, on this study site, this E horizon has been completely removed due to plowing and erosion, and a Ap plowing horizon is surfacing.

An Eutric cambisol, as encountered at the backslope position (Figures 2.5 and 2.6) is characterized by the very beginning phase of soil weathering in the subsoil. This transformation of the parental material, increasing the clay percentage and the partial removal of initial carbonates content (WRB, 2014), led to the formation of a structural B horizon (Bw, as indicated by the AbB Belgian classification on Figure 2.6). This Bw horizon is a medium texture material (i.e. here loess silt with a progressive enrichment in clay in the subsoil), with low weathering level of the parental material (i.e. justified here by the presence of CaCO_3), leading to the absence of appreciable quantities of illuviated clays and Al and/or Fe compounds (WRB, 2014). Here, a high base saturation (i.e. > 50%) associated with a basic pH justifies the Eutric qualifier (WRB, 2014).

A colluvic Regosol (Figure 2.7. b), as encountered both at the toeslope and footslope positions (Figures 2.5 and 2.6), is a very weakly developed soil in unconsolidated material, not made of sands or fluvic materials, and often found in accumulation zones of eroding lands (WRB, 2014). Hence, no profile development and no diagnostic horizons are observed due to its young age (WRB, 2014), as indicated by the Abp Belgian classification in Figure 2.6.

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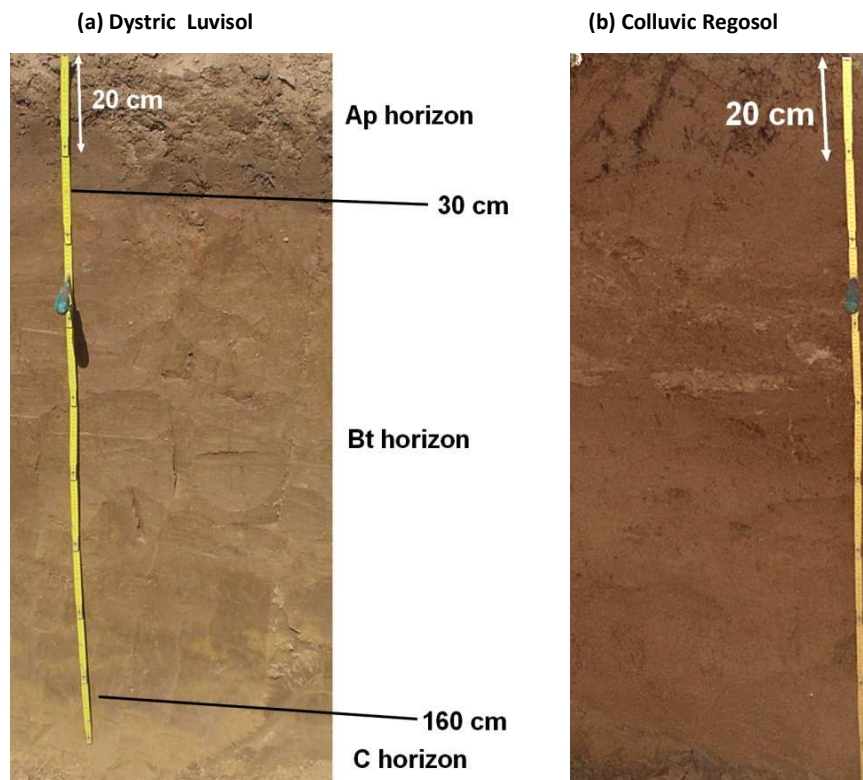


Figure 2.7. Pictures of the soil profiles and of their diagnostic horizon (if any) on our study site: (a) the Dystric Luvisol at the summit; (b) the Colluvic Regosol at the footslope.

2.3. Overall experimental setup

An experimental setup has been installed along the hillslope (Figure 2.7). This experimental setup was used for several in-situ experiments and provided the observations presented and discussed in chapters 3 to 7. This section provides a global overview of the sampling design, all experiments together.

The following variables were monitored in time: soil surface CO₂ fluxes, soil profiles of CO₂ concentration, soil surface and soil profile volumetric water content, and soil surface and soil profile temperature. Some variables were supposed not to vary with time during the 3 studied years, and were thus measured only once: soil OC concentration, soil IC concentration, soil porosity, soil bulk density, soil texture.

Surface CO₂ fluxes were monitored at the five slope positions. A portable infrared gas analyzer with an automated closed dynamic chamber (LI-8100A system, LI-COR, UnitedStates) was used to measure soil surface CO₂ fluxes according to the methods described in Davidson et al. (2002). On all five slope positions, six collars (20 cm diameter) were installed at the soil surface for CO₂ fluxes measurements, inside an area of 5 meters long and 3 meters wide (Figure 2.8).

Soil surface temperature (0-10 cm depth) was measured with a T-handled type-E thermocouple sensor (8100-201, LI-COR, UnitedStates) at the five slope positions.

Soil surface volumetric water content (VWC) was measured (in the upper 6 cm of the soil profile) using a portable five-rod 0.06 m long FDR (frequency domain reflectometry) probe system (ML2x, Delta-T, UnitedKingdom) at the five slope positions.

In the framework of another PhD research on the same site (Tran et al., 2014), Ground Penetrating Radar (GPR) field campaigns were conducted to characterize the **space-time variability of soil moisture at the soil surface** (Figure 2.7). The GPR system consists of a vector network analyzer (ZVNA,

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Rohde & Schwarz, Munich, Germany) connected to a broadband horn antenna, to a differential global positioning system device (DGPS) (Leica GPS1200, Leica Geosystems, Heerbrugg, Switzerland), and mounted on a 4-wheel motorcycle. The results of these latest measurements are not presented in this thesis.

Soil CO₂ concentrations profiles (Figure 2.8 and 2.9) were measured at both the summit and the footslope positions by means of specific designed soil CO₂ probes. The CO₂ sensor in the probe is based on the CARBOCAP® Single-Beam Dual Wavelength non-dispersive infra-red (NDIR) technology (GMM221, Vaisala corp., Vantaa, Finland). These probes were inserted in a perforated PVC tube, based on the technique presented by Young et al. (2009). These tubes were inserted vertically into the soil, after augering holes with a diameter that equals the diameter of the PVC tubes (Figure 2.8).

Soil temperature along soil profiles (Figure 2.8 and 2.9) was monitored at both the summit and the footslope positions using a thermistor probe (Therm107, Campbell Scientific Lt., UK).

Soil VWC along soil profiles (Figure 2.8 and 2.9) was monitored at both the summit and the footslope positions using Time Domain Reflectometry (TDR) probes.

Water, temperature and CO₂ concentration profiles measurements were recorded with an automatic data logger (CR1000, Campbell Scientific Lt., UK) (Figure 2.7, 2.8 and 2.9), connected to a multiplexer (AM16/32, Campbell Scientific, Campbell Scientific Lt., UK) to increase the number of input channels (Figure 2.9).

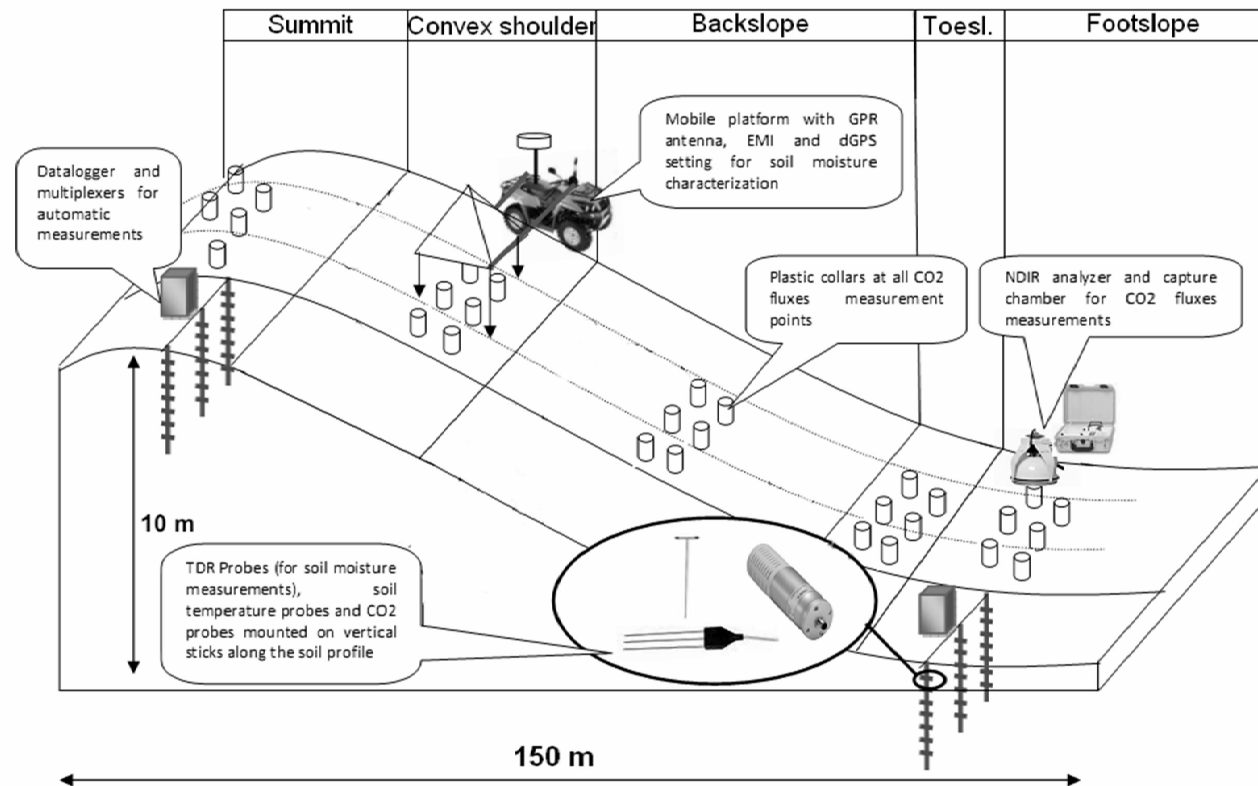


Figure 2.7. Schematic description of the experimental setup all along the hillslope.

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Soil properties along soil profiles were characterized at the beginning of the research (2011) using replicated one meter long soil cores (spaced 3 to 5 meters from each other) at the 5 slope positions. Some of these cores were extracted using a pneumatic auger, while others were manually extracted from a 2.5 meters deep soil pit (Figure 2.9). These soils pits were used as well for the description of the diagnostic horizons (19 slope positions spaced c.10 meters from each other along the hillslope, from the summit to the valley bottom).

In order to avoid vegetation growth and autotrophic contribution to respiration, the plots were covered with a synthetic permeable geotextile during the complete measurement period (Figure 2.9). This allows isolation of the impact of environmental variables (e.g. soil moisture and temperature) on the mineralization rate of soil OC.

All these **probes were calibrated** before using it. Most of them were calibrated in factory and provided with a calibration certificate, while TDR probes were calibrated by our-self in the laboratory, as explained in details in chapter 7 of this thesis.

The measurements frequency depends on each studied variable. The soil surface measurements (further details in chapter 4 of this thesis) were carried out on 34 days between spring 2010 and winter 2012. The measurement campaign resulted in an experimental database of 1342 observations (34 days, 5 slope positions, c.4 space-replicates, 2 time-replicates). The profile measurements (further details in chapter 7 of this thesis) were carried out at an hourly frequency in 2012 from 12 May to 13 December at the footslope and from the 2nd of June until the 13 December at the summit, and in 2013 from 14 May at the summit and 14 June 2013 at the footslope until 22 November 2013 at the two stations. In 2012, some CO₂ measurements were not always possible due to sensors failures and unsuitable measurement range of some sensors.

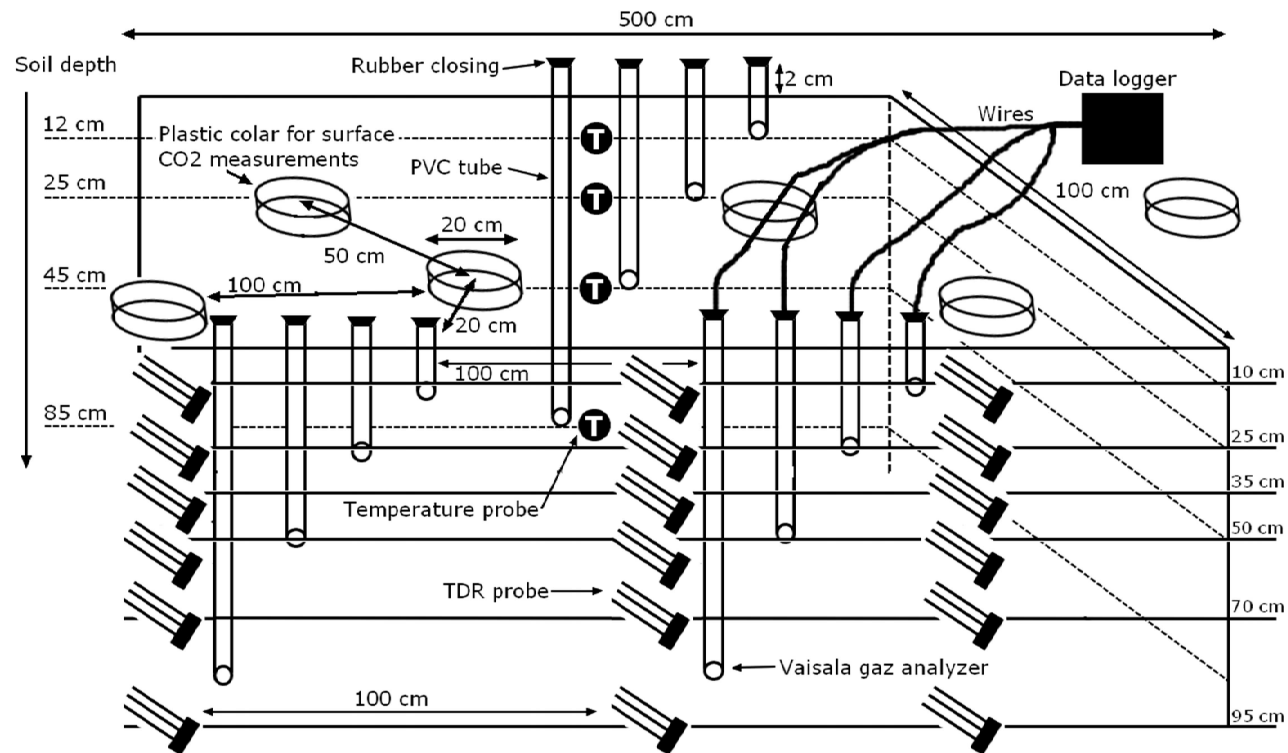


Figure 2.8. Schematic description of the experimental plot (sampling design) at both the summit and the footslope positions.

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Figure 2.9. Picture of the installation phase of an experimental plot (summit position): (a) all soil probes are connected to a wiring box with multiplexer, dataloggers and batteries; (b) a soil pit has been dug until c. 2.5 meters depth to allow probes installation (i.e. for soil moisture and temperature); (c) after filling the pit, the surface of the measurement station is covered by a geotextile, collars for surface CO₂ fluxes are installed, and probes for profile CO₂ measurements are inserted vertically.

3. The spatial distribution of soil organic carbon quality¹

3.1. Introduction

Soil processes play a key role in the global C cycle by regulating soil-atmosphere C exchange through soil organic carbon (OC) production and mineralization. Recently, researchers have highlighted the need to consider soils as mobile systems (Quinton et al., 2010). Soil erosion - and the resulting lateral fluxes of soil OC and sediment along hillslopes- has been identified as a significant process affecting the soil system and soil OC dynamics, particularly on agricultural land (Jacinthe and Lal, 2001; Lal, 2003; Berhe et al., 2012).

New insights into erosion processes and their impact on OC dynamics have been derived from mass-balance and model studies (e.g. Van Oost et al., 2005a; Smith et al., 2005), but the influence of soil erosion on the C cycle is still associated with high uncertainties. Contradictory assertions have been proposed about whether hillslope can be considered as net C sources or C sinks (Manies et al., 2001; Van Oost et al., 2007). There is now increasing awareness

¹ Adapted from the following peer-reviewed publication:

Wiaux, F., Cornelis, J.T., Cao, W., Vanclooster, M., Van Oost, K. (2014). Combined effect of geomorphic and pedogenic processes on the distribution of soil organic carbon quality along an eroding hillslope on loess soil. **Geoderma** 216, 36-47.

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that approaches are needed which explicitly consider the linkages between geomorphological processes, operating at the scales of landscapes, and local pedogenic processes, operating at the pedon-scale (e.g. Berhe et al. 2007, 2008, 2012). Three key mechanisms that link erosion with OC dynamics, acting together or separately, have been identified (Stallard, 1998; Van Oost et al., 2007): (i) replacement of eroded OC at eroding sites through continued OC inputs from new photosynthate and plant litter decomposition (Stallard, 1998; Harden et al., 1999), (ii) burial of carbon in low mineralization contexts at sites of deposition (Stallard 1998), and (iii) enhanced decomposition of OC as a result of the chemical and physical breakdown of soil during detachment and transport (Lal, 2003; Berhe et al., 2012). However, a full mechanistic understanding of the effect of erosion and burial processes on soil OC dynamics is still lacking.

In most models of OC dynamics (e.g. Bauer et al., 2012), OC decomposition is controlled by: (i) the initial OC amount; (ii) OC quality, defining the intrinsic decomposition rate; and (iii) environmental conditions (e.g. temperature, access to water, to oxygen, and to micro-organisms). The latter can be considered as reduction or amplification factors of the intrinsic mineralization rate, which reflects the potential mineralization of OC in relation to its quality. OC decomposition can be described by equation 1.1 (chapter 1).

Soil OC quality can be defined as the ability of OC to supply organic molecules and to release carbon dioxide through metabolic pathways. This implies that low quality OC corresponds to OC molecules that require a high number of enzymatic steps to release CO₂ (e.g. Kleber and Johnson, 2010; Dungait et al., 2012).). It is suggested that low quality OC is related to the strong chemical inter-molecular interactions of OC with reactive mineral phases (von Lutzow et al., 2006; Kögel-Knabner et al., 2008b; Dungait et al., 2012). In this study, we use this concept to define high and low quality OC, as further detailed in chapter 1, section 1.1.2.

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Furthermore, and in agreement with eq. 3.1, recent studies have shown that OC quality alone does not control the long-term stability of soil OC but that environmental and biologic controls are also important (Marschner et al., 2008; Kleber and Johnson, 2010; Schmidt et al., 2011; Dungait et al., 2012; Berhe and Kleber, 2013). For example, Schmidt et al. (2011) reported that old OC can be of high quality while Berhe and Kleber (2013) suggested that the stability of a substrate in a specific ecosystem could change considerably when deposited in a system with different micro-climatic or environmental conditions. In the context of global climate change, understanding the spatial and temporal variability of soil OC quality and erosion-induced lateral fluxes of OC between systems characterized by different environmental conditions are thus important to predict present-day and future soil OC stability (Berhe et al., 2007, 2008, 2012; Doetterl et al., 2012). Berhe et al. (2012) demonstrated that soil erosion can lead to reconfiguration of organo-mineral associations influencing the distribution of soil OC pools along a hillslope. Nadeu et al. (2012) showed that eroded OC at the catchment-scale was buried and stabilized at the depositional site, but argued that the rate of replacement of eroded OC is likely not be equally distributed over different OC pools. However, these studies focused on natural ecosystems, which are characterized by very low erosion rates and high Net Primary Production relative to disturbed agro-ecosystems (Berhe et al., 2012; Nadeau et al., 2012). Based on physical fractionation methods, Doetterl et al. (2012) studied the distribution of OC pools along an agricultural hillslope taking into account short-term stabilization processes such as aggregation. At present, the combined geomorphic and pedogenic effects on OC quality distribution and OC stabilization by organo-mineral associations on agricultural land remain poorly quantified.

In this study, we address this issue by quantifying the spatial variability of OC quality (as defined above) in relation to geomorphic and pedogenic processes on a cropland subjected to high rates of erosion. Our objectives are: (i) to quantify the spatial variability in OC quality in relation to soil erosion along a slope catena on a cultivated loamy soil; and (ii) to identify the underlying

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geomorphic and pedogenic mechanisms. Finally, we discuss the implications of our findings in relation to soil OC stabilization processes.

3.2. Materials and methods

3.2.1. Site description

The study site and the overall experimental set-up have been described in details in chapter 2.

3.2.2. Soil samples

At each slope position, replicated soil cores (spaced 3 to 5 meters from each other) were collected. The number of replicates that were used in the analysis varied with depth, with $n=4$ to 6, $n=3$, $n=3$, $n=4$, for the 0-30 cm, 30-40 cm, 40-60 cm, 60-100 cm depth layers respectively. Some of these cores were extracted using a pneumatic auger, while others were manually extracted from a soil pit. For the diagnostic horizons method (see further), soil pits with a depth of 3 meters were used. All samples were directly frozen after collection. Before analysis, the samples were air-dried, passed through a 2 mm sieve and crushed before analyses. At each slope position, samples were also collected at 10 cm depth intervals in a soil pit. These samples were used for the analysis of soil texture and bulk density (with 4 replicates at each depth) using 100 cm³ metal cylinders.

3.2.3. Soil analyses

3.2.3.1. Soil physico-chemical properties

For texture and pH analyses, samples were pretreated following the ISO11464 method. pH was obtained with electrode measurements. Samples used for texture analysis were dispersed using a Na₂CO₃ and sodium exametaphosphate solution. Granulometric analyses for clays and silt were then performed according to the Robinson pipette method (AFNOR-NF X 31-107 norm) with a

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Texsol24B (LCA Instruments, France) sedimentation automaton. The sand fraction was obtained by wet sieving at 50 μm . The 100 cm^3 samples used for the bulk density measurements were oven dried at 105°C during 48 h and then weighted. The bulk density was then calculated as the ratio between the sample weight and its volume. The reported value is the mean of 4 samples collected at the same depth.

3.2.3.2. Reactive soil minerals

Si, Fe and Al were extracted using acid ammonium oxalate at pH 3 (oxalate extraction) and sodium pyrophosphate at pH 10 (Dahlgren, 1994) using a dithionite-citrate reagent buffered by sodium bicarbonate (DCB extraction) (Mehra and Jackson, 1960). Mineral concentrations were then quantified using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Instrument precision for elemental concentration (Al, Fe and Si) is 0.05 g/kg. Both amorphous Fe and Al-oxyhydroxides and poorly crystalline aluminosilicates, assessed by the concentration of Al, Fe and Si in the oxalate-extractable solutions (Si_{ox} , Al_{ox} , and Fe_{ox}), were used as indicators of mineral soil reactivity in relation to OC stabilization (Torn et al., 1997): amorphous and poorly crystalline mineral components have a high chemical capacity (e.g. hydroxyl functional groups) to establish covalent links with organic matter (von Lutzow et al., 2006; Kleber et al., 2007) under the form of Mineral-Protected OC (MP-OC) (Mikutta et al., 2005a). This kind of OC stabilization has been shown to reduce the susceptibility of OC to oxidative attack (Kögel-Knabner et al., 2008a). As mineral reactivity depends on both pH conditions and the activity and valence of ions in the soil solution (Schwertmann and Taylor, 1989), the oxalate extraction alone does not provide a quantitative measurement but is only an indicator of the soil capacity to stabilize soil OC through the formation of organo-mineral associations.

FeDCB represents both crystalline and poorly crystalline Fe oxyhydroxides. The Fe activity ratio ($\text{Fe}_{\text{ox}}/\text{Fe}_{\text{DCB}}$) consequently reflects the poorly crystalline fraction of total Fe oxides (Schwertmann and Taylor, 1989) and can be used as an indicator of the degree of soil minerals weathering (Mikutta et al., 2005a).

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Crystalline and poorly crystalline iron oxides are characterized by high and reactive specific surface compared to other clay-size minerals like kaolinite, smectite, illite, etc. Therefore, in some environments, the interactions between Fe oxyhydroxides and OC can control a large part of the OC stabilized (Oades et al., 1988; von Lutzow et al., 2006; Kögel-Knabner et al., 2008b; Kaiser et al., 2012).

The extractions of Si, Fe and Al were carried out for one single soil core for each slope position. Due to problems in laboratory analyses, we could not obtain replicates for these extractions. Hence, in order to allow statistical comparisons between slope positions, measurements were grouped into two soil depths classes, i.e. the 0-30 cm soil layer (n=2) and the 30-100 cm soil layer (n=3). To that aim, for each of these two soil depths classes, we used paired t-test (contrasts matrix allowing two by two comparisons between slope positions), processed in the free software R.

3.2.3.3. Organic carbon

Before OC analysis, plant debris and discrete particulate organic matter were removed by liquid flotation using water (1 g cm^{-3}). This procedure may have induced some loss of cold water-extractable OC (CWEOC). However, the quantity of CWEOC can be neglected as it represents a very small fraction of the total OC (Marinari et al., 2010; Choudhary et al., 2013). Total C (i.e. the sum of organic and inorganic C) was analyzed using the dry combustion technique (Variomax elemental analyzer, Elementar GmbH). Instrument precision for total C analyses is 0.05% C concentration. The samples were then treated with 1% HCl in order to remove inorganic CaCO_3 and were analyzed again with the elemental analyzer. CaCO_3 and OC concentration was then deduced from the difference between total carbon analyses before and after 1% HCl treatments.

A variety of analytical methods are available to characterize OC pools in soils (Six et al., 1998, 2002; Mikutta et al., 2005; Siregar et al., 2005; Mikutta et al., 2006; von Lutzow et al., 2007; Kögel-Knabner et al., 2008a; Berhe et al., 2008). Although we are still far away from a broadly accepted fractionation protocol,

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one of the most commonly used methods is based on chemical oxidation using reagents such as H_2O_2 , NaOCl , KMnO_4 and $\text{Na}_2\text{S}_2\text{O}_8$. This kind of method relies on the preferential removal of more chemically labile OC (Mikutta et al., 2005b; von Lutzow et al., 2007; Kögel-Knabner et al., 2008a). Among those methods, NaOCl attack (pH 8) was reported to be one of the most efficient and reliable to isolate a stable OC (NaOCl -resistant OC), without dissolving pedogenic oxides (Siregar et al., 2005; Mikutta et al., 2005b; von Lutzow et al., 2007). In summary, no single fractionation technique fully describes the stabilization of soil OC. However, Sleutel et al. (2011) presented empirical evidence supporting the notion that the OC pool isolated through oxidation in NaOCl is related to soil OC stability (defined as the inverse of OC “mineralizability”).

In our study, stable OC was defined as the pool of NaOCl -resistant OC (Siregar et al., 2005). We quantified the stable OC by mixing 3 g of air dried soil with 30 ml of 6 wt % NaOCl (adjusted to pH 8). The NaOCl -treated soil was then washed (shaken and centrifuged) with de-ionized water until the solution was chloride free (i.e. no reaction with AgNO_3 occurred). The samples were then dried at 105°C and homogenized before collecting a subsample for total C measurement by dry combustion. The labile OC pool was defined as the residual OC pool that was not resistant to NaOCl oxidation. Hence, this labile OC pool should be interpreted as easily mineralizable OC under ideal conditions where no other factors play a role in stabilization (e.g. anoxic environment, aggregation, etc). The proportion of labile OC was obtained by a simple ratio between labile OC amount and total OC amount.

3.2.4. SOC stock

We used the following formula (eq. 3.1) for the calculation of SOC stocks (Goidts et al., 2009):

$$\text{SOC stock} = \frac{d * C * BD * [1 - RM]}{1000} \quad (\text{eq. 3.1})$$

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where SOC stock is the soil OC stock (kg.m^{-2}), d the thickness of the soil layer represented by the sample considered (m), C the soil OC concentration (g kg^{-1}), BD the soil bulk density (kg m^{-3}), and RM the mass proportion of rock fragment content. Given that no rock fragments were observed in this study site, RM was set to zero. For each sample depth, a soil OC stock was then calculated using the bulk density and mean OC values calculated according to section 2.2, as well as pedogenic information to assess the limits between soil layers. The soil OC stock for each slope position was then estimated by integrating eq. 3.2 over depth.

3.2.5. Erosion quantification

In order to relate OC quality with erosion processes, we quantified cumulative erosion and deposition along the toposequence using two complementary approaches: (i) a method based on diagnostic horizons that quantifies erosion and deposition since the start of agriculture and (ii) a method based on the fallout radionuclide ^{137}Cs that provides estimates of erosion and deposition for the last 5 decades. Short-term cumulative erosion depth was obtained by this latest method. Long-term cumulative erosion depth was calculated as the difference between cumulative erosion depth given by the diagnostic horizons method (section 2.5.1) and cumulative erosion depth obtained by ^{137}Cs inventories (short-term erosion, section 2.5.2).

3.2.5.1. Diagnostic horizons method

One meter long soil cores were sampled at 19 slope positions spaced c.10 meters from each other along the hillslope (from the summit to the valley bottom). On each of those soil cores, the depth to the calcareous loess was measured based on a HCl test. This approach resulted in a quantitative estimate of the spatial distribution of historical erosion along the hillslope, as described by Rommens et al. (2005). A reference depth of $230 (\pm 12)$ cm has been used for the upper level of the calcareous horizon for uneroded profiles in the region studied here (Brahya et al., 2000; Rommens et al., 2005; Van Oost et al., 2005). The underlying assumption is that pedogenesis has resulted in a

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spatially uniform decalcification of the loess in the landscape (Brahya et al., 2000; Rommens et al., 2005).

3.2.5.2. ^{137}Cs Caesium inventories method

The artificial fallout radionuclide $^{137}\text{Caesium}$ (^{137}Cs), deposited at the soil surface in the 1950s after nuclear bomb-fallout events, has been used for short-term soil erosion assessment (i.e. at decadal time-scales) (Walling & Quine, 1990; Quine, 1995). The concentration of the tracer (in mBq/g) in the upper 80 cm of each soil core was measured in the Environmental Radionuclide Laboratory of the University of Exeter (UK). Concentrations were then converted into inventories (Bq/m^2) using the soil depth and bulk density values (Table 3.1). ^{137}Cs variability along the transect was then analyzed by applying a mean filter ($n=3$). This was done to remove small-scale variability and to detect the general pattern. Six reference cores were sampled and analyzed on a nearby uneroded plateau (grassland since at least 60 years). Two of these cores were excluded, as they largely exceeded the maximum ^{137}Cs radioactivity fallout observed in this region (Vanden Berghe and Gulinck, 1987). The mean reference value used in this study (based on 4 observations), was then $2102 (\pm 151) \text{ Bq/m}^2$. The conversion of ^{137}Cs inventories into erosion and deposition rates for the period 1954-2011 was done using the proportional method (Quine, 1995).

3.3. Results

3.3.1. Soil erosion assessment and physico-chemical properties distribution

The depth of the calcareous loess decreases from the upper summit position to the backslope, where calcareous material is mixed within the plough layer (Table 3.1). We estimate that c. 1.3 m of soil has been removed from the convex shoulder position since the start of agriculture. This resulted into a partial removal of the Bt horizon. At the backslope position, c. 2.3 m of soil was

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eroded and this completely removed the Bt horizon. This denudation resulted in the surfacing of the unweathered and calcareous soil parent material (Table 3.1). As a result of erosion, c. 35% of the hillslope now contains CaCO₃-rich soil material in the surface layer. A fraction of the eroded material was deposited at the bottom of the hillslope on top of an uneroded profile and this formed a colluvial soil profile of c. 1 m thick.

The observed ¹³⁷Cs inventories are shown in Figure 3.1. A significant effect of slope position on ¹³⁷Cs inventories has been demonstrated by a statistical regression ($p < 0.01$). The highest rates of short-term (i.e. last 5 decades) soil erosion are found at the convex shoulder position (30 ± 7 cm), while 15 ± 2 and 15 ± 15 cm of soil was recently (last 5 decades) eroded at the summit and at the backslope, respectively. During these last 5 decades, an accumulation of sediment was observed at the footslope position (30 ± 20 cm) (Table 3.1).

The texture is relatively homogeneous with depth and along the hillslope (c. 20% clay, 75% silt, 5% sand), except for the 80 cm and 100 cm depth interval at the backslope position, where the sand percentage reaches 64.5% (see Table 3.1). The sand fraction was slightly higher within the 60 first cm of the footslope and backslope positions (c. 10% vs. 5% at the other slope positions). pH_(KCl) values (Table 3.1) show that soil profiles at the summit position are acidic (pH 6.2-6.4), at the convex shoulder position near-neutral (pH 6.6-7.1), at the backslope position clearly basic (pH 7.4-7.7), and at the footslope basic at the surface and more acidic with depth (pH from 6.6 at 1 m depth to 7.4 at the soil surface).

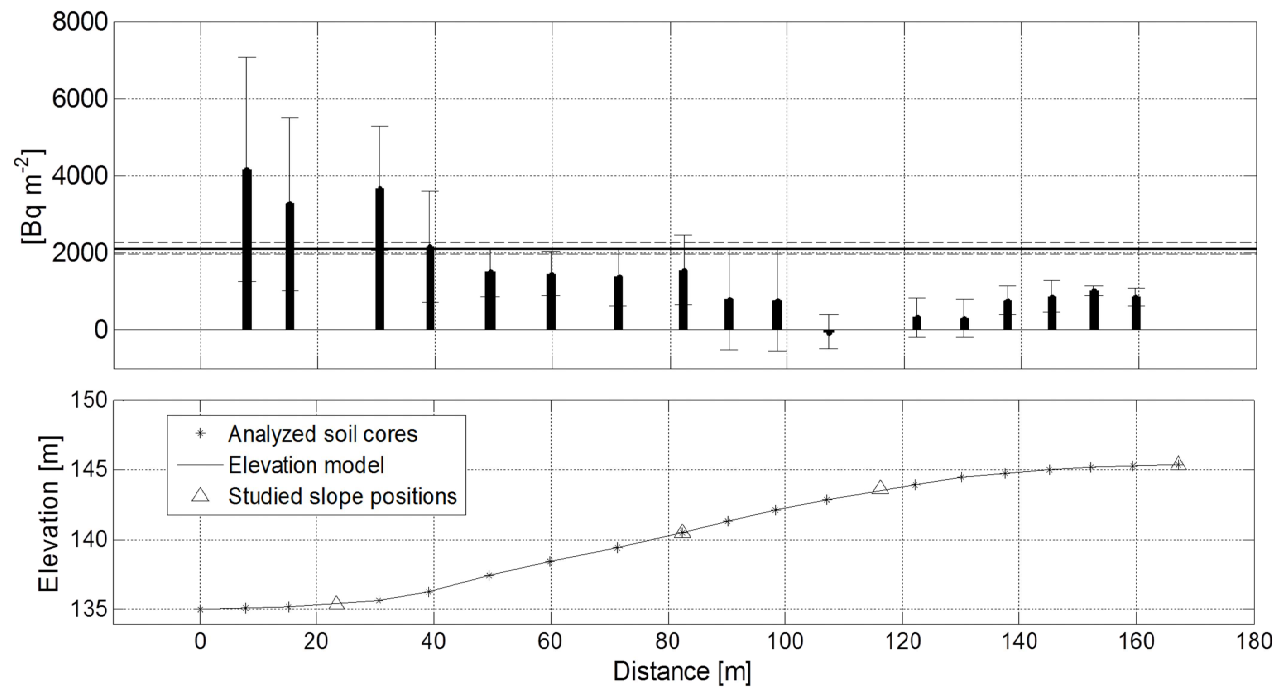


Figure 3.1 Observed ^{137}Cs inventories along the hillslope. The inventories are smoothed by using a moving average of 3 neighbouring profiles. The full line represents the reference value of an uneroded grassland plateau ($2102 \pm 151 \text{ Bq/m}^2$). Error bars reflect the standard deviation around the mean at each slope positions (moving average based on 3 observations).

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Table 3.1. Soil physico-chemical properties along the hillslope. Numbers in brackets are standard deviation (SD). “/” indicates that no information is available for this parameter. “Wat” and “Till” mean water and tillage erosion, respectively.

Cumulative erosion and deposition (-) [cm]	Depth (cm)	Hr.	Texture [%]				Bulk density (g/cm ³)	pH KCl	CaCO ₃ (g/Kg)			
			clay		Silt		sand					
Wat.	Till.											
Reference theoretical uneroded summit: Dystric Luvisol												
(Brahya et al., 2000; Rommens et al., 2005)												
0	0-7	Ah	13.3	/	71.0	/	15.7	/	0.93	/	/	/
	7-33	E	13.1	(±1.1)	75.1	(±2.8)	11.8	(±1.7)	1.37	/	/	/
	33-150	Bt	19.4	(±0.9)	68.6	(±3.0)	12	(±2.1)	1.61	/	/	/
	150-230	BC	17.5	/	71	/	11.5	/	/	/	/	/
	>230	C	15.1	/	66.9	/	14.8	/	1.51	/	/	/
Summit (our study): Dystric Luvisol												
45	0-30	Ap	21.3	(±0.8)	73.3	(±1)	5.3	(±0.2)	1.45	(±0.01)	6.4	0.0 /
	30-40	Bt	19.8	/	76	/	4.2	/	1.61	(±0.05)	6.2	0.0 /
	40-60	Bt	19.6	(±2.5)	74.3	(±1.3)	6.2	(±1.2)	1.54	(±0.06)	6.3	0.0 /
	60-100	Bt	19.3	(±0.5)	74.4	(±0.5)	6.3	(±0.3)	1.52	(±0.03)	6.4	0.0 /
Convex shoulder (our study): Dystric Luvisol												
100	0-30	Ap	20.4	(±0.3)	73.5	(±1.1)	6.1	(±1.1)	1.55	(±0.09)	7.1	1.1 (±0.0)
	30-40	Bt	21	/	74.4	/	4.6	/	1.51	(±0.05)	6.6	0.0 /
	40-60	Bt	21.2	(±0.7)	72.5	(±1.7)	6.3	(±1)	1.51	(±0.02)	6.6	0.0 /
	60-100	Bt	18	(±1.3)	75.4	(±1.9)	6.6	(±0.9)	1.48	(±0.05)	7	0.0 /
Backslope (our study): Dystric Cambisol												
>215	0-30	Ap	19.7	(±0.5)	68.3	(±2.3)	11.9	(±2)	1.55	(±0.09)	7.6	3.9 (±1.0)
	30-40	C	16.5	/	76.4	/	7	/	1.47	(±0.05)	7.7	5.3 (±2.1)
	40-80	C	16.4	(±0.7)	73.1	(±5)	10.5	(±4.4)	1.43	(±0.05)	7.7	5.3 (±1.4)
	80-100	Sand	18.2	(±1)	17.3	(±13.4)	64.5	(±14.1)	1.42	(±0.05)	7.4	0.0 /
Footslope (our study): Colluvic Regosol												
-70	0-30	Ab	17.4	(±0.1)	71.1	(±0.6)	11.5	(±0.7)	1.50	(±0.06)	7.4	1.9 (±0.2)
	30-40	Ab	17.5	/	71.9	/	10.6	/	1.59	(±0.06)	7.7	1.6 (±0.1)
	40-60	Ab	18.4	(±1.6)	73.6	(±0.8)	8	(±0.7)	1.58	(±0.04)	7	0.6 (±0.1)
	60-100	Ab	20.1	(±2.2)	75.3	(±2.4)	4.6	(±0.9)	1.59	(±0.03)	6.6	0.0 /

3.3.2. Soil OC pool & stock distribution

On Figure 3.2a, we can observe that the total OC stocks (0-1m) are variable along the hillslope. Although no significant differences are observed between the convex shoulder and the summit position, the footslope and the backslope positions are different from the other positions in terms of their OC stocks. More specifically, the footslope has a significantly higher (c. 2.5 times, $p < 0.01$) amount of total OC ($9.0 \pm 1.0 \text{ kg OC m}^{-2}$) and labile OC ($5.8 \pm 0.2 \text{ kg OC m}^{-2}$), when compared to the other slope positions. The backslope shows a significantly lower amount of NaOCl-resistant OC, c. 2 times lower ($1.4 \pm 0.4 \text{ kg OC m}^{-2}$) than at the footslope, the convex shoulder and the summit positions ($p < 0.05$, $p = 0.12$ and $p = 0.15$, respectively).

Figure 3.2b shows the relative proportion of each OC pool in the total OC stock. The proportion of labile OC is $64 \pm 5\%$ and $69 \pm 5\%$ at the footslope and the backslope positions, respectively, while it represents only $40 \pm 22\%$ and $49 \pm 6\%$ at the convex shoulder and summit positions, respectively. These differences in labile OC stock proportions are significantly different ($p < 0.05$), especially when comparing the two eroded slope positions. Indeed, at the backslope position, the NaOCl-resistant OC proportion is c. 30%, while it is two times higher (c. 60%) at the convex shoulder ($p < 0.1$).

3.3.3. Soil OC depth profiles

The OC pool distribution with depth is further detailed in Figure 3.3. The total OC concentrations are significantly higher ($p < 0.001$) at the footslope position than at the other slope positions, for all depths, with the exception of the 0-30 cm soil layer, where soil OC has been homogenized by tillage operations. Labile OC concentration is significantly higher from 30 to 100 cm depth at the footslope position (as well as between 0 and 40 cm at the backslope position), than at the summit and the convex shoulder positions ($p < 0.05$). The proportion of labile OC is significantly higher at the footslope position (30-60 cm), and at

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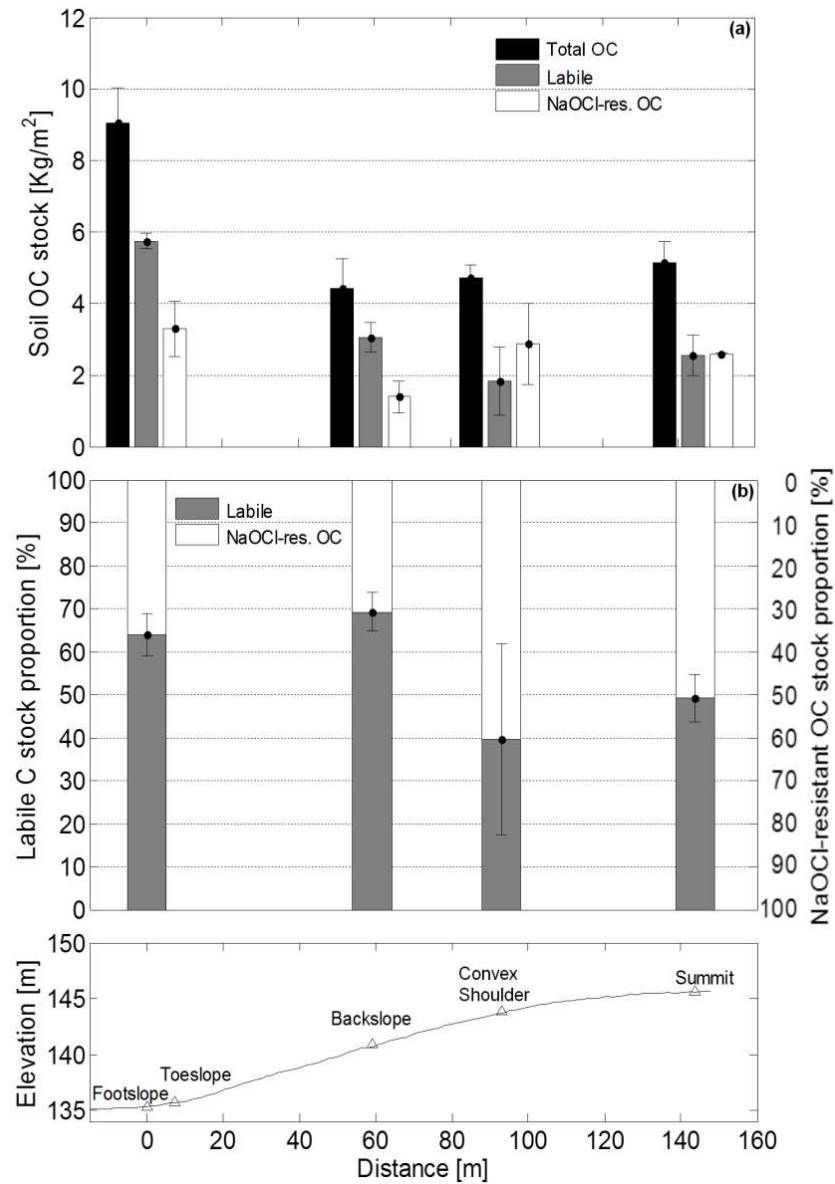


Figure 3.2. (a) Mean stocks (0-1m) of soil OC-pools at different slope positions (error bars indicate 1 standard deviation with $n=3$); (b) Proportion (relative to Total OC) of labile OC and NaOCl-resistant OC stocks (0-1m) at different slope positions.

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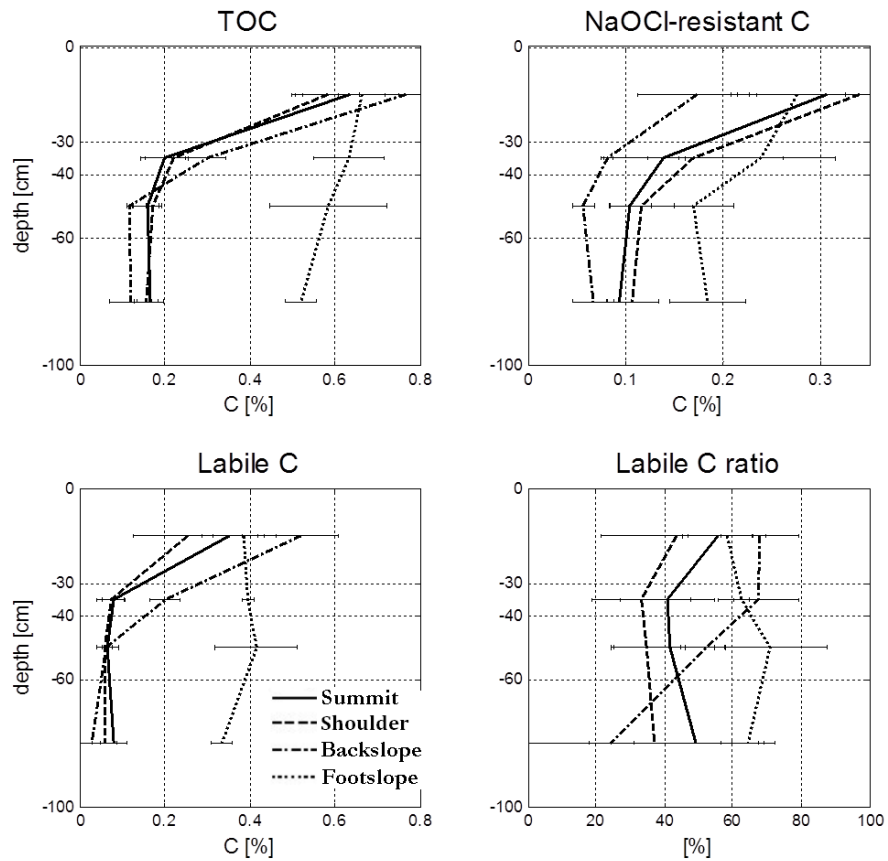


Figure 3.3. Soil profiles (0-100 cm) of OC pools (C%), and their relative proportion (Labile C ratio, in %) at different slope positions. Error bars indicate 1 standard deviation (n≥3).

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the sub-surface of the backslope position (30-40 cm), when compared to the summit and the convex shoulder positions.

Figure 3.3 also shows that NaOCl-resistant OC concentrations at the soil surface (0-30 cm) are significantly lower at the backslope position when compared to the convex shoulder and summit positions at the same depths ($p < 0.1$). The concentration of NaOCl-resistant OC at the footslope (60 - 100 cm) is higher than at other slope positions ($p < 0.01$).

These results indicate that the OC pool distribution (i.e. labile OC versus NaOCl-resistant OC) is strongly differentiated along the hillslope. The foot- and back-slope positions contain a higher amount and a higher proportion of labile OC.

3.3.4. Al and Fe oxyhydroxides

A multiple regression analysis (Table 3.2) showed that NaOCl-resistant OC is correlated with the soil reactive phases (amorphous Al- and Fe- oxyhydroxides, reflected by elements concentration in the oxalate extraction (Fe-ox and Al-ox)). The specific effect of Al- and Fe- oxyhydroxides on the amount of NaOCl-resistant OC (Table 3.2) was found to be significant. Among these mineral species, Fe oxyhydroxides explained the highest part of the variability of NaOCl-resistant OC values ($R^2 = 83\%$), followed by Al oxyhydroxides ($R^2 = 79\%$). Notice that when considering a single regression model with the combined effect of oxalate-extractable Al, Fe and Si, only the effects of Fe and Si are significant. For this case, we observed a negative effect of oxalate-extractable Si (used here as an indicator of poorly crystalline aluminosilicates).

The data were further analyzed by normalizing NaOCl-resistant OC by the amount of clay available at each depth. These results confirm that the correlation between OC and soil reactive phases is due to specific minerals that OC can associate with, and not only to an increased mineral surface area due to higher clay content. However, NaOCl-resistant OC was not correlated to elements concentration in the DCB extraction (reflecting crystalline Iron oxides). At the backslope position, Fe and Al oxyhydroxides decrease with

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depth (Figure 3.4). For all the other slope positions, Fe and Al oxyhydroxides are relatively constant within the surface layer (0-30 cm) and the subsoil (30-100 cm).

This observation suggests that mean values per position, where observed concentrations are averaged over these two depths, can be used to test for differences between slope positions (Figure 3.5). For both depth layers, Fe-ox and Al-ox contents are significantly lower ($p < 0.01$ and $p < 0.001$, respectively) at the backslope position than at the other positions (Figure 3.5). Al-ox content is significantly higher at the convex shoulder position than at the other positions, especially the backslope position. Both at the surface (0-30 cm) and in the subsoil (30-100 cm), the mean Fe-ox and Al-ox contents are about 2 times higher at the convex shoulder positions than at the backslope position (Figure 3.5). The backslope has therefore significantly lower contents in Fe-ox and Al-ox, relative to other slope positions, reflecting a lower exposure age of the loess material and a consequently shorter time for pedogenesis.

The lower Fe activity ratio ($\text{Fe}_{\text{ox}}/\text{Fe}_{\text{DCB}}$) at the backslope relative to the other slope positions (Figure 3.6) reflects a lower degree of soil mineral weathering (Mikutta et al., 2005a), especially at the soil surface (0-30cm). The Fe activity ratio is an indicator for the degree of soil weathering (Burstein, 1997; Mikutta et al., 2005a). The differences in Fe activity ratio are particularly visible at the soil surface (0-30cm), but are also present for the entire soil profile. These observations are consistent with the lower contents in Fe-ox and Al-ox observed above and are indicative for a younger soil (i.e. exposed to pedogenesis for a shorter time) at the backslope position.

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Table 3.2. Multiple regression analysis between NaOCl-resistant OC (Stable OC), total OC (TOC), and Al, Fe and Si from the oxalate extraction solution (Alox, Feox and Siox, respectively) in g/kg.

Regression model	Significance of the different variables					Coefficient of determination
	Fe _{ox}	Al _{ox}	Fe _{ox} +Al _{ox}	Si _{ox}	TOC	
StaOC=0.07Alox+0.26 TOC	/	**	/	/	***	R ² =79%
StaOC=0.04Feox+0.20 TOC	***	/	/	/	***	R ² =83%
StaOC=0.12Siox+0.28 TOC	/	/	/	**	***	R ² =74%
StaOC=0.08Feox+0.18 TOC-0.14Siox	**	n.s.	/	.	***	R ² =86%
StaOC=0.06(Feox+Alox)+0.20 TOC-0.18Siox	/	/	**	*	***	R ² =86%
n.s.=not significant						
. Significant on the 0.1 probability level						
* Significant on the 0.05 probability level						
** Significant on the 0.01 probability level						
*** Significant on the 0.001 probability level						

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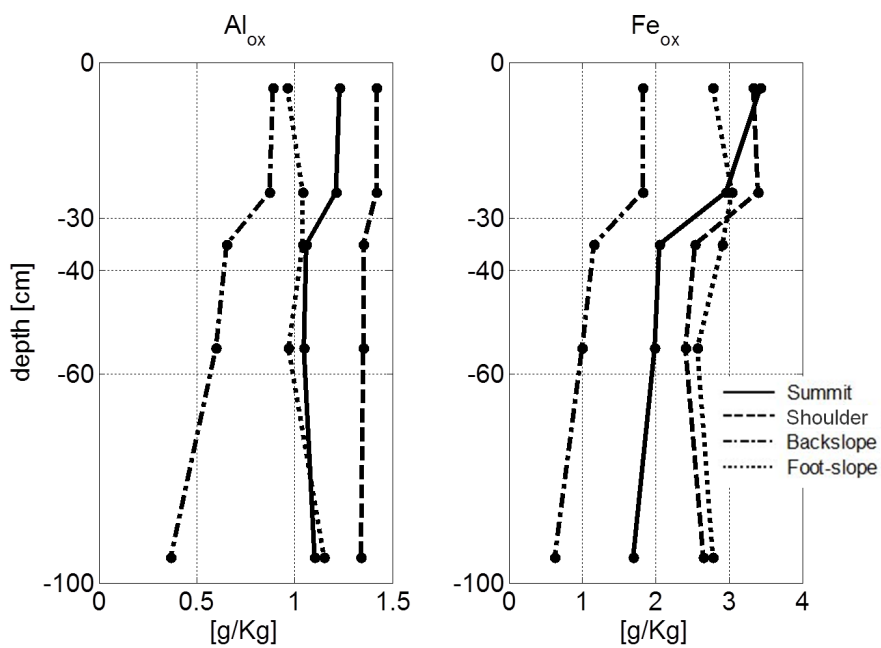


Figure 3.4. Soil profiles (0-100 cm) of Al and Fe oxi-hydroxides (g/kg), obtained by measuring the concentration in the oxalate extraction solution, at different slope positions.

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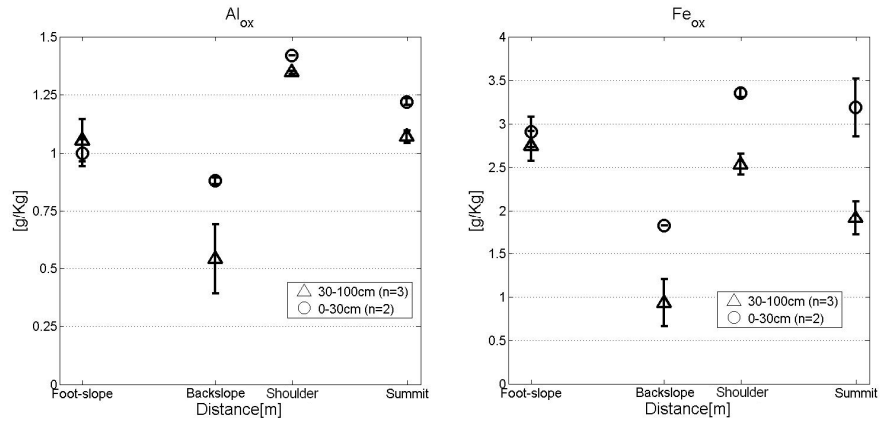


Figure 3.5. Average percentages and standard deviation, within the soil surface (0-30 cm, n=2) and within the subsoil (from 30 cm to 1 m depth, n=3) of amorphous Aluminium oxides (Al_{ox} , left) and amorphous Iron oxides (Fe_{ox} , right).

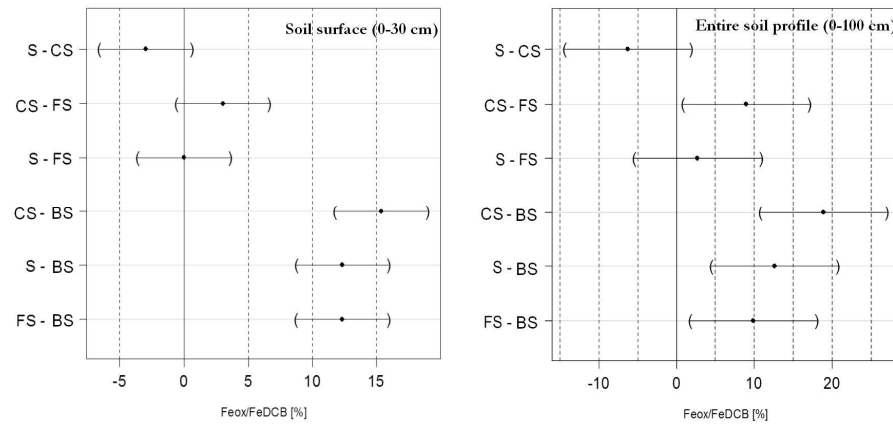


Figure 3.6. Comparison two slope positions by two slope positions (95% confidence level) of the ratio between amorphous Iron oxides from the oxalate solution (Fe_{ox}) and total Iron oxides from the DCB solution (Fe_{DCB}); Left: within the soil surface (0-30 cm, n=2); Right: along the entire soil profile (from 0 cm to 100 cm depth, n=5); S=Summit; BS=Backslope; MS=Midslope; FS=Footslope.

3.4. Discussion

3.4.1. Soil erosion and deposition

Our results show that the hillslope was exposed to intensive soil erosion, leading to a transfer of soil material from the summit and the slope to the footslope. At the backslope position, c. 2 m of soil was removed and the calcareous parent material can be found directly below the surface layer. The convex shoulder position experienced less erosion and is characterized by a cumulative soil truncation of c. 1.3 m. Based on the ^{137}Cs analyses, we identified a switch of the location where the most intensive erosion took place along the hillslope before and after the 1950s, i.e. from the backslope to the convex shoulder position. This switch has related to the introduction of mechanized agriculture and acceleration of tillage erosion (Van Oost et al., 2005b).

Comparing the different soil profiles of the hillslopes (Table 3.1) with a reference and uneroded profile that developed on loess soils under forest (Brahy et al., 2000; Rommens et al., 2005), we can observe that organo-mineral Ah and eluvial E horizons have been completely removed by erosion along the hillslope. The erosional history of the backslope and convex shoulder positions has resulted in different soil properties: intensive erosion at the backslope position led to the rejuvenation and resurfacing of calcareous parent material over an area of c. 45 meters at the backslope position. In contrast, and as a result of lower rates of erosion, soils are slightly truncated at the convex shoulder and summit positions where the Bt horizon has only been partially removed. Despite higher rates of soil erosion at the convex shoulder since the 1950's, the Bt horizon has only been removed partially and the calcareous parent material is not surfacing. However, notice that if erosion due to mechanized plowing continues at the same rate ($0.5 \pm 0.1 \text{ cm year}^{-1}$ at the convex shoulder position, obtained by dividing short-term cumulative erosion by 50 year), calcareous loess soil will reach the surface in c. 200 years, not only around the backslope position, but along the entire hillslope, causing important

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damages in terms of yield production due to the much lower fertility of the calcareous C horizon, as suggested by Reyniers et al. (2006).

Deposition of the eroded material resulted in the formation of a colluvial soil at the footslope position. Given the spatial patterns of long- and short-term erosion, we can safely assume that this colluvium was formed mainly by soil particles originating from the backslope position, while more recent deposits (since the 1950's) may also contain material from the convex shoulder position. This interpretation is further supported by the pH data (Table 3.1): at the footslope, going from basic values in the plow layer to acidic values at 1 m depth (with a neutral boundary at c. 50 cm depth). This pH profile shows that old deposits, now found at the bottom of the colluvial profile, are decalcified and were likely eroded from a decalcified soil profile. In contrast, younger deposits coming from the backslope (now found at the upper part of the colluvial profile, upper 50 cm) contain CaCO_3 as they were eroded from a profile where the calcareous parent material was surfacing. Note that this interpretation is based on the assumption that pH values can be considered as a conservative tracer. Hence, pH cannot be used alone to support this interpretation. However, it corroborates our other findings about soil particles translocations along the hillslope.

3.4.2. The quality of soil OC stored in the colluvium

Our results showed a significant larger labile OC stock at the footslope position (colluvium). The relative proportion of labile OC was also higher at both the footslope and the backslope positions (Figure 3.3) than at the other slope positions. The colluvium formed at the footslope by the transfer and burial of soil material from the eroded slope is thus significantly enriched in labile OC. We observed no statistical differences between the slope positions for the surface layer (i.e. 0-30 cm), but this can be explained by the homogenization of the surface layer by plowing.

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The high stock and relative percentage of labile OC (c. 70%) at the footslope (0-1m profile) suggests a high potential mineralization rate at this position. However, these results do not allow considering the footslope as ineffective at storing C, as the OC stabilization is mainly dependent on the specific environmental conditions at this position (Schmidt et al., 2011, Bauer et al., 2012), and not only on OC quality. The large soil total OC stock ($9.0 \pm 1.0 \text{ kg OC m}^{-2}$) found at the footslope then suggests that environmental and physical factors are likely to play a more important role in the stabilization of OC. This supports the statement of Schmidt et al. (2011) that soil OC stabilization must be considered as an ecosystem property, and that its quality does not necessarily reflect its actual fate. However, the high potential of mineralizability of OC stored at the footslope is key to assess hillslope behavior under different environmental conditions. The buried OC stock in colluvial soils could be easily converted to CO_2 given its high quality. For instance, the magnitude and the frequency of dry events may increase because of climate change (IPCC, Fowler et al. 2005), and such dry events have been shown to enhance the contribution of deep soil layers to OC mineralization (Carlisle et al. 2006). Our results suggest that buried OC in colluvial settings is particularly prone to such events.

As far as physical protection mechanisms (e.g. soil micro-aggregates) are concerned, these are likely to play an important role in the stabilization of OC at depositional sites (Doetterl et al., 2012). However, physical stabilization is not a permanent process (Krull et al. 2003; von Lützow et al., 2006; Kögel-Knabner et al., 2008b). Doetterl et al. (2012) showed that only 14% of the fast pool, 43% of the intermediate pool and 32% of the passive pool are preserved after burial and long-term decomposition processes. This indicates that buried OC is only partially protected by this physical mechanism (e.g. Van Oost et al., 2012), and supports the statement that different stabilization mechanisms operate at different timescales (von Lützow et al., 2006). The OC stabilized by spatial inaccessibility (e.g. occlusion in soil aggregates) has been shown to decompose much faster (typical residence times of c. 1-100 years) than organic molecules stabilized by strong molecular interactions with mineral surfaces (typical residence times of c. 100-1000 years) (von Lützow et al., 2006).

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3.4.3. OC quality distribution along the hillslope

3.4.3.1. Combined geomorphic and pedogenic effect

The high correlation between NaOCl-resistant OC and amorphous and poorly crystalline reactive soil minerals, strongly suggests that the NaOCl-resistant OC pool corresponds to a Mineral Protected OC pool (MP-OC), as already showed by Mikutta et al. (2005a). These organo-mineral associations are related to strong molecular interactions between hydroxyl functional groups of Fe and Al-oxyhydroxides and hydrophobic poles of organic matter (von Lutzow et al., 2006; Kleber et al., 2007). Mikutta et al. (2005a) reported similar regression models with strong correlation between NaOCl-resistant OC and Fe, Al and Si concentrations in the oxalate solution from Luvisols and Cambisols. Here, the correlation between NaOCl-resistant OC and Fe_{ox} alone displays higher R^2 values (83%) than in the study of Mikutta et al. (2005a) (56%). When considering Fe_{ox} , Al_{ox} and Si_{ox} all together, Mikutta et al. (2005a) found slightly higher R^2 values (94%) than this study (86%). Note that the negative correlation of Si concentration in the oxalate extraction solution with NaOCl-resistant OC that we observed in this study can be explained by a competitive behavior of Si_{ox} with OC for sorption on Fe oxyhydroxides (Mikutta et al., 2005a).

The MP-OC content is significantly lower at the backslope position when compared to the other slope positions. At the backslope position, only 30% of the total OC stock (0-1m) is strongly stabilized with soil minerals, while the proportion of MP-OC is 60% and 50% at the convex shoulder and the summit positions, respectively. This corroborates the substantially lower amount in reactive soil phases (such as Fe-Al oxy-hydroxides) at the backslope position compared to the other slope positions, as shown on Figure 3.4 and 7.

Combining these pedogenic mechanisms within a geomorphologic framework, it is possible to understand the distribution of OC quality along the hillslope. Although both the convex shoulder and backslope positions have been eroded, the unweathered calcareous loess, which is very poor in reactive secondary clay minerals, is only present at the surface of the backslope. As a consequence, the

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convex shoulder and summit positions are characterized by weathered decalcified loess, where an important pool of reactive neo-formed minerals is present (Figure 3.4-7). This results in Fe- and Al- oxyhydroxides contents which are about 2 times higher at the convex shoulder and summit positions than at the backslope position (Figure 3.5). At the footslope, Fe- and Al- oxyhydroxides contents are as high as at the convex shoulder and summit positions. This can be explained by the transfer and burial of soil material from the eroded slope. This indicates that oxide stocks at the different slope positions are explained by both weathering level and erosional transport. This higher weathering status of the convex shoulder and the summit positions, relative to the backslope, has been demonstrated by the significantly lower Fe activity ratio at the backslope (Figure 3.6).

This suggests that the higher proportion of labile OC at the soil surface of the eroded backslope are related to the erosion and rejuvenation of the soil profile by bringing unweathered calcareous loess towards the soil surface. Due to the lower Fe- and Al- oxyhydroxides contents, the stabilization processes through organo-mineral associations will be less important at the backslope. Our data thus suggest that the replacement of the eroded OC (Stallard 1998; Harden et al., 1999) is not equally distributed over the different OC pools. At slope positions where unweathered soil material (typically poor in reactive soil minerals) is brought to the surface, a high proportion of labile OC can be expected. The enriched labile OC pool at the backslope position induced by pedogenic conditions will also affect the quality of the OC found at the footslope, as this is the sediment source area. This may explain why the same proportion of labile OC stock is found both at the footslope and at the backslope ($64 \pm 5\%$ and $69 \pm 4\%$, respectively), and why this proportion is significantly higher at these positions than at the convex shoulder and summit ($40 \pm 22\%$ and $49 \pm 6\%$, respectively).

The proportion of MP-OC is significantly lower at the footslope compared to the convex shoulder and summit positions. However, the amount of reactive minerals (Fe- and Al- oxyhydroxides) at the footslope is as high as at the convex

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shoulder and summit positions. These two observations can be reconciled by using the concept of soil OC saturation described in recent studies (Six et al., 2002; von Lützow et al., 2006; Stewart et al., 2007). This suggests that soils have an upper limit to their capacity to stabilize and store OC. In other words, we argue that the important input of labile OC at the footslope exceed the capacity of Fe- and Al- oxyhydroxides to stabilize it. This excess of non-chemically stabilized OC is likely to accumulate in soils (e.g. because of specific environmental conditions) without being directly mineralized, which explains the very large proportion of labile OC at the footslope all along the soil profile, despite the high amount of soil reactive minerals.

3.4.3.2. Uncertainties in the explanation of OC pools distribution along the hillslope

So far, we have not considered the effect of spatial differences in plant production and hence OC input along the hillslope. For example, a higher plant primary productivity at the footslope, due to a higher nutrient status, could also explain the observed enrichment of the labile pool. However, biomass measurements on a similar slope transect in our study area clearly showed that plant biomass was substantially lower on the backslope and footslope positions (Reyniers et al., 2006). At the backslope, the unweathered and calcareous topsoil is not very fertile and leads to lower yield and biomass production (Reyniers et al., 2006). Despite the accumulation of eroded sediments enriched in nutrients and organic matter at the footslope, yields are relatively low. This is related to a more compacted soil and very wet conditions that lead to anaerobic conditions. As a result, observed yields at both the backslope and footslope positions were two times lower than at the summit and convex shoulder positions (Reyniers et al., 2006). Hence, if variability in plant primary productivity controls the spatial pattern of the OC pool distribution along the hillslope, the foot- and convex shoulder positions should contain less labile OC. This is not consistent with our observations and we therefore conclude that the spatial variability in OC input is not an important factor and that erosion and deposition processes predominate. Note that we assume proportionality

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between aboveground biomass production and belowground OC inputs. Hence, like for aboveground biomass, OC inputs coming from roots decomposition should neither play an important role in OC stock distribution along the hillslope.

Another explanation for the observed differences in OC quality could be the lower residence time of soil material at eroded slope positions. Indeed, long periods of time (100-1000 years) are needed to form stable humic substances and organo-mineral associations (von Lutzow et al., 2006). The higher amount and proportion of MP-OC that we observed at the summit (Fig. 3.1-4) is consistent with a longer residence time of OC at this position, as soil particles are not subject to up- or downwards advection as a result of erosion or deposition. At both the backslope and the convex shoulder positions, soil OC has a smaller residence time given the higher erosion rates at these positions compared to the summit position (Table 3.1). In rapidly eroding profiles, the new photosynthate has no time to stabilize through the pedogenic processes such as humification, adsorption and complexation (von Lutzow et al., 2006). Our assessment of erosion (Table 3.1) showed that the backslope and the convex shoulder were both strongly eroded during a long period of time. We therefore expect lower MP-OC concentrations at these positions. However, this is not supported by our observations (Figure 3.2). Assuming a period of cultivation of c. 500 year and by taking the observed long-term cumulative erosion rates (Table 3.1), we can estimate the residence time of soil material in the surface layer (0-30 cm). The residence time of soil particles at the soil surface are then c. 75, 150 and 300 years for the backslope, convex shoulder and summit positions, respectively. The residence time at the surface (0-30cm) of the backslope is then c. 2 times lower than at the convex shoulder. However, this is not reflected in the proportion of MP-OC and we found no direct relationship between residence time and observed OC pool distribution. As a consequence, soil residence time as an indicator for OC ability to react with soil minerals fails to explain the observed OC distribution along our hillslope.

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We therefore argue that the main factor controlling the OC quality distribution along the hillslope is the rejuvenation of the unweathered subsoil layers poor in reactive secondary minerals at the most eroded slope position.

High uncertainties remain about the amorphous and poorly crystalline reactive soil minerals, due to the low number of analyzed soil samples and the absence of spatial replicates. We recommend paying a particular attention to avoid such methodological limitations in future researches on this topic. Also, note that some uncertainties exist about the functional link between NaOCl-resistant OC and amorphous and poorly crystalline reactive soil minerals. Indeed, while we showed that those two soil chemical fractions are highly correlated, this correlation in itself does not constitute an evidence of the functional impact of reactive soil minerals on OC stabilization. Among other things, the higher amount of reactive soil minerals and of NaOCl-resistant OC could be both explained by the higher amount of accumulated soil particles at the bottom of the slope coming from eroded soil surface along the hillslope. However, we argue that this “amount” effect (impact of soil quantity on NaOCl-resistant OC amount) should have been isolated from the functional link between reactive soil minerals and stable OC by having considered the amount of total OC in the statistical regression (Table 3.2.). In addition, NaOCl-resistant OC pool has already been showed to correspond to a Mineral Protected OC pool (MP-OC) by other studies (e.g. Mikutta et al., 2005a).

Finally, in such quasi-neutral or lightly carbonated environments (Table 3.1), the role of base cations (e.g. Ca^{2+} and Mg^{2+}) in organo-mineral associations cannot be excluded. Some slope positions (backslope and some parts of the footslope profile) have a significant inorganic carbon content (Table 3.1), and all the slope positions are within the ideal pH range for OC stabilization by cation bridges (i.e. pH 6.5 to 7.5, according to Kaiser et al. (2012)). However, the bonding efficiency between OC and minerals by cation bridges is weaker relative to the stronger ligand exchange between OC and Al and Fe-oxyhydroxides (von Lutzow et al., 2006). OC stabilized by weak cation bridges could therefore be considered as part of the labile OC pool (these OC pools

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segregation are at some extent arbitrary, as OC pools actually form a continuum from more labile to more stable quality). In fact, part of the OC stabilized by cations bridges can be partly dissolved by the NaOCl attack method used in this study, and consequently, may not have been considered as part of the MP-OC pool (Mikutta and Kaiser, 2011). As a consequence, the high proportion of labile OC detected at both the backslope and the footslope positions may be partly protected by the cation bridges mechanism, and the labile OC stocks would have a lower potential of mineralization than expected. NaOCl oxidation is often used to mimic OC oxidation by enzymes of soil micro-organisms. Although this method may not decompose exactly the same OC pool than soil micro-organisms, NaOCl-resistant OC remains a good indicator of the OC quality, even if it may decompose a lightly more or less resistant OC pool than soil micro-organisms do.

In any case, the mineralization potential of the OC stocks at both the backslope and the footslope positions has been shown to be higher than the mineralization potential of the OC found at the other slope positions. Given that the role of base cations is likely to be spatially uniform (because of the small range of pH values), we argue that the possible effect of cation bridges will not affect this main conclusion of this study.

3.5. Summary and conclusion

Our analysis of an eroding hillslope in the Belgian Loess Belt showed that colluvial (depositional) soils store a large amount of OC ($9.0 \pm 1.0 \text{ kg OC m}^{-2}$; 0-1m depth), and contain up to twice more OC than stable or eroding slope positions. We also demonstrated that these depositional soils contain a significantly higher proportion of labile OC (c. 70% in the labile pool at the footslope, compared to c.40 and 50% at the convex shoulder and summit positions, respectively). As a consequence, and regardless of the environmental conditions that may have resulted in its stabilization, the high quality of this colluvial OC stock suggests a high potential mineralization rate. In some specific environments, soils may store a large stock of potential volatile carbon (Dungait

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et al., 2012). The significant enrichment of the labile OC pool at the footslope relative to other slope positions observed here has implications when assessing the potential stability of the soil OC stock in response to future change in environmental conditions (e.g. induced by climate change).

Secondly, we found that ongoing erosion has resulted in a low amount of reactive soil phases (mainly, Al- and Fe-oxyhydroxides) in the upper first meter of the most eroded soil profile (backslope position). We suggest that this is related to the erosion and rejuvenation of the soil profile by bringing unweathered calcareous loess towards the soil surface. In other words, erosion has a substantial impact on the OC pool distribution when a threshold is reached. This threshold corresponds to the resurfacing of unweathered subsoil layers low in reactive mineral content. As a result of the lower amount of reactive soil phases at the backslope position, the potential to stabilize OC by molecular interactions with soil minerals or by physical occlusion into nano-scale clay microstructures is reduced, relative to other slope positions. This implies that mineral-protected OC plays a minor role at the backslope relative to other eroded slope positions, in terms of quantity (1.4 ± 0.4 , 2.9 ± 1.1 and 2.6 ± 0.6 kg OC m⁻² at the backslope, convex shoulder and summit positions, respectively) and in terms of proportion (31 ± 4 %, 60 ± 22 % and 51 ± 6 % at the backslope, convex shoulder and summit positions, respectively). The colluvium formed at the footslope by the transfer and burial of soil material from the eroded slope is thus also significantly enriched in labile OC.

The high proportion of labile OC detected at both the backslope and the footslope positions may also be weakly protected by cation bridge mechanisms, typical of near-neutral and carbonated soils. Despite the contribution of this specific stabilization mechanism were not quantified here, this does not change the general trends of OC distribution showed in this study. We conclude that the combined geomorphic and pedogenic effects on soil properties largely control soil OC quality along an eroding hillslope.

4. Factors controlling soil organic carbon persistence¹

4.1. Introduction

Current approaches for quantifying OC turnover in soils are typically informed by 1-D vertical modeling concepts that focus on the understanding of soil OC turnover in flat, non-sloping landscapes. The large spatial heterogeneity of factors that control soil OC respiration in sloping landscapes, where process interactions and feedback are significant, is thus not fully considered in current models of soil OC dynamics (Chaopricha and Marín-Spiotta, 2014; Trumbore and Czimczik, 2008). In contrast to flat lands, sloping landscapes exhibit strong spatial gradients in soil OC storage, water and temperature (e.g. Schimel et al., 1985), and this may have a strong influence on OC turnover and ultimately on the overall landscape C balance (Martin and Bolstad, 2009; Webster et al., 2008b). In addition, erosion along hillslopes has been shown to enhance the

¹Adapted from the following peer-reviewed publication:

Wiaux, F., Vanclooster, M., Cornelis, J.T., Van Oost, K., 2014. Factors controlling soil organic carbon persistence along an eroding hillslope on the loess belt. **Soil Biology and Biochemistry** 77, 187-196.

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temporal variability of soil OC dynamics (Van Oost et al., 2005) and to generate a heterogenic distribution of soil OC quantity and quality along hillslopes (Berhe et al., 2012; Doetterl et al., 2012; Nadeuet al., 2011; Schimel et al., 1985; Wiaux et al. 2014a - chapter 3 of this thesis). Furthermore, the heterogeneity of soil respiration cannot be easily decoupled from the underlying pedological gradients (Davidson et al., 1998;Epron et al., 2006). As a result, there is an increasing awareness that geophysical, geomorphic and biogeochemical approaches must be combined to determine OC persistence and dynamics within landscapes (Berhe and Kleber, 2013; Chaopricha and Marín-Spiotta, 2014).

Surface heterotrophic respiration fluxes can be used as an indicator for the persistence of soil OC (e.g. Gregorich et al., 1994). Recently, several observational studies have quantified soil respiration fluxes along hillslopes, but a clear consensus on the controlling factors and process interactions is still lacking. Some studies reported higher respiration rates at footslope positions, relative to summit and shoulder positions (Reicosky et al., 2005; Webster et al., 2008b), but opposite trends were also reported in Epron et al. (2006) and Wang et al. (2013). In contrast, other studies did not detect differences in soil CO₂ respiration along hillslopes (e.g. Fiener et al., 2012). These inconsistencies are likely related to the following issues. First, different methodological (e.g. laboratory incubation vs. insitu field measurements) and statistical (e.g. additive vs. multiplicative model) approaches were employed. Second, isolating the specific heterotrophic (i.e. soil microbial) respiration from the autotrophic (i.e. plant root) respiration is not straightforward (e.g. Davidson et al., 1998; Epron et al., 2006; Luan et al., 2013; Martin and Bolstad, 2009; Webster et al., 2008b). Hence, the significant uncertainties associated with the discrimination between autotrophic and heterotrophic respiration may mask spatial differences in soil heterotrophic respiration across the landscape (e.g. Fiener et al., 2012). Third, the range of measured soil volumetric water content (VWC) values observed in some studies is relatively narrow (e.g. from 10 to 18% VWC in Martin and Bolstad, 2009; from 12 to 16% VWC in Pingintha et al., 2010; from 19 to 35% VWC in Fiener et al., 2012). It is possible that this narrow

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range may not be sufficient to fully and accurately capture its effect on soil respiration. Fourth, in-situ respiration studies are confronted with an inherent difficulty in quantifying the role of single factors for a flux that is largely controlled by interacting processes (e.g. soil water and temperature, Akinremi et al., 1999; Davidson et al., 1998; Herbst et al., 2008; Howard and Howard, 1993; Perrin et al., 2004).

In addition, the sensitivity of soil OC to temperature (as expressed by Q₁₀ values) can vary along hillslopes. Despite the fact that there is increasing awareness that OC stabilization is to a large extent controlled by environmental factors (e.g. Kögel-Knabner et al., 2008; Schmidt et al., 2011), the effect of abiotic factors on the temperature sensitivity of soil OC has rarely been discussed in the literature. Conant et al. (2011) reviewed the impact of OC quality on Q₁₀, but the impact of soil VWC (which varies along hillslopes) on temperature sensitivity still needs to be explored.

In this study, our main objective is to identify the controls on soil OC persistence along a loamy hillslope. We used surface heterotrophic soil respiration measurements as an indicator of the inverse of this OC persistence. More specifically, we aim (i) to study the factors controlling OC persistence under real-life conditions using in-situ measurements and (ii) to assess if these controls on OC persistence are permanent in time and space, by exploring OC temperature sensitivity along the hillslope. Finally, we discuss our results in relation to OC persistence and to changes under varying seasonal (short-term) and climatic (long-term) conditions.

4.2. Materials and methods

4.2.1. Site description

The study site and the overall experimental set-up have been described in details in chapter 2.

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4.2.2. Surface CO₂ fluxes and abiotic variables

Soil surface CO₂ fluxes, soil volumetric water content and soil surface temperature were measured at the five slope positions. A portable infra-red gas analyzer with an automated closed dynamic chamber (LI-8100A system, LI-COR, United States) was used to measure soil surface CO₂ fluxes according to the methods described in Davidson et al. (2002). In order to avoid vegetation growth and autotrophic contribution to respiration, the plots were covered with a synthetic permeable geotextile during the complete measurement period. This allows isolation of the impact of environmental variables (e.g. soil moisture and temperature) on the mineralization rate of soil OC. Soil volumetric water content was measured at the soil surface (upper 6 cm of the soil profile) using a portable five-rod 0.06 m long FDR (frequency domain reflectrometry) probe system (ML2x, Delta-T, United Kingdom). Soil surface (0-10 cm depth) temperature was measured with a T-handled type-E thermocouple sensor (8100-201, LI-COR, United States). Volumetric water content was converted to water-filled pore spaces (WFPS) using porosity values. Porosity was measured on intact soil cores (100 cm³ sample volume) by comparing weights after water saturation and after oven drying.

On all five slope positions, six collars (20 cm diameter) were installed at the soil surface inside an area 5 meters long and 3 meters wide (Fig.1). At each slope position, the collars were installed with a distance between 1.1 to 5 meters from each other in order to quantify the small-scale spatial variability. Each soil surface CO₂ flux measurement was repeated twice. Measurements were carried out on 34 days between spring 2010 and winter 2012 (Figure 4.3). Measurement campaigns were c. 3 hours long. As a consequence of this long duration of measurement campaigns, temperature variations can induce significant variation in soil respiration (Fiener et al., 2012). This time-dependent temperature trend was removed afterwards (see section 4.2.4). In addition, measurements were not systematically carried out at the same time of the day depending on the availabilities of the technician team and on the meteorological conditions. Therefore, the CO₂ flux was standardized at a

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common reference temperature for each day to allow comparisons between days and between slope positions (see section 4.2.4).

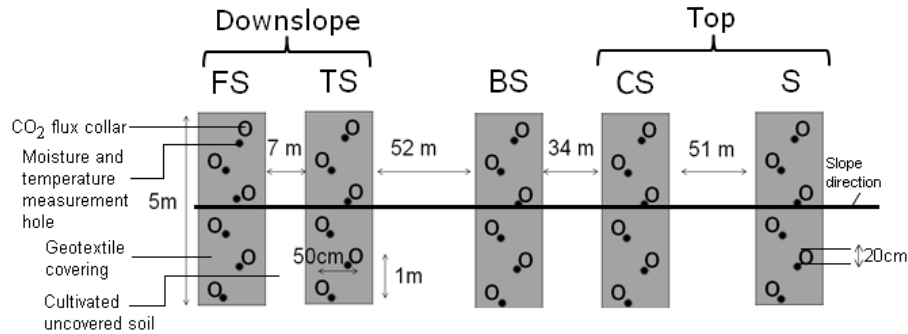


Figure 4.1. Soil surface respiration sampling design for each slope position (plan view): footslope (FS), toeslope (TS), backslope (BS), convex slope (CS), summit (S).

For each day and each slope position, a filter was applied to remove observations displaying inconsistent values relative to the mean CO₂ flux measurement value. These erroneous observations were mainly due to technical measurement problems (e.g. wind, batteries, chamber locking, incomplete chamber aeration, etc.). The measurement campaign resulted in an experimental database of 1342 observations (34 days, 5 slope positions, c.4 space-replicates, 2 time-replicates).

4.2.3. Soil organic carbon

We use the OC stock and quality data presented in the study of Wiaux et al. (2014a, chapter 3 of this thesis) which was conducted on the same hillslope and slope positions. In short, at each slope position, soil profile samples (spaced 3 to 5 meters from each other) were collected (3 to 4 replicates), and analyzed for total C, OC, labile OC, bulk density (BD) and porosity. The labile OC pool was defined as the residual OC pool that was not resistant to NaOCl oxidation (Siregar et al., 2005; Sleutel et al., 2011) and can be considered as easily mineralizable OC under ideal conditions where no other factors play a role in stabilization (e.g. anoxic environment, aggregation, etc.) (Wiaux et al., 2014a -

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chapter 3 of this thesis). For statistical analyses, soil OC stocks were calculated for the entire soil profile (0-1m depth).

4.2.4. Statistical analyses

We used a multiple regression model to test the effects of abiotic factors on soil surface respiration fluxes. For all statistical analyses, a Generalized Least Square (GLS) model was applied in R-2.14.0 for Windows (R Development Core Team, 2007). Due to the small distance between collars, CO₂ fluxes data at a given slope position cannot be considered as independent samples (Aiken et al., 1991; Herbst et al., 2009). For measurements taken on the same slope position and same day, this spatial correlation was taken into account. To this end, we defined a correlation structure (compound symmetry type) for the error terms of the model as described in Pinheiro and Bates (2000).

The statistical regression model used in this study is conceptually coherent with physical processes governing CO₂ production. It is based on a priori knowledge, derived from published studies on the relationships between abiotic variables and soil respiration (e.g. Bauer et al., 2012). Consistent with the literature, we considered that OC decomposition results from a multiplicative effect between OC stock, OC quality, and environmental conditions (temperature, access to water, to oxygen, and to micro-organisms). In order to be consistent with the bimodal behavior of soil respiration in response to soil water content, as reported in the literature (e.g. Bauer et al., 2012; Perrin et al., 2004), statistical regression was applied on two sub-data sets, i.e. dry (<57% WFPS) and wet (>57% WFPS) conditions. As the respiration flux increases exponentially with soil temperature following the Arrhenius equation (Fang and Moncrieff, 2001; Perrin et al., 2004; Winkler et al., 1996), the conceptual model has the following form for each of the two water content sub-data sets (Eq. 4.1):

$$R_s = a \text{ LOC } ^b Q_{10}^{\left(\frac{T-15}{10}\right)} \text{ WFPS}^{\text{cat}} \text{ WFPS}^c \quad (\text{Eq. 4.1})$$

where R_s is the heterotrophic respiration flux [$\mu\text{mol m}^{-2} \text{ s}^{-1}$], LOC is the amount of labile (easily mineralizable) soil OC [kg.m^{-2}], WFPS is the soil water content

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expressed in terms of Water Filled Pore Space (WFPS) [$\text{m}^3 \text{ m}^{-3}$], T is the soil temperature [$^{\circ}\text{C}$], Q_{10} [-] is the parameter that represents the increase of soil respiration caused by a temperature increase of 10°C (Perrin et al., 2004; Winkler et al., 1996), and a , b and c are model parameters defining the strength of these effects. In order to account for the synergetic effect of soil temperature and soil water content, the response of respiration flux to soil temperature was modeled separately for different water content categories (WFPS cat.). More precisely, we divided the “wet” sub-dataset into three equal size water content categories (57-68%, 68-80%, >80% WFPS).

In order to obtain a normally distributed dataset (which is necessary for the parametric method used here) and to transform the regression model into an additive linear model, we used a logarithmic transformation (Eq. 4.2):

$$\ln(R_s) = \ln(a) + b \ln(\text{LOC}) + \ln(Q_{10}) \left(\frac{T-15}{10} \right) \text{WFPS.cat.} + c \ln(\text{WFPS}) \quad (\text{Eq. 4.2})$$

In a first stage, we used this model (Eq. 2) as a tool to identify the controls on soil heterotrophic respiration. In a second stage, parameters values derived from the regression were used to successively remove the effect of temperature (i.e. dividing R_s by $Q_{10}^{\frac{T-15}{10}}$), temperature and soil OC (i.e. dividing R_s by Labile OC $^b Q_{10}^{\frac{T-15}{10}}$), temperature and soil water content (i.e. dividing R_s by $Q_{10}^{\frac{T-15}{10}} \text{ water content}^c$). For wet conditions, time - and hence temperature - variation during measurement campaigns (c. 3 hours long) can induce significant variation in soil respiration (Fiener et al., 2012). Our regression model allowed us to accurately evaluate this time-dependent temperature trend based on the entire data base, and then to remove this temperature effect (standardization at 15°C) to allow further comparisons between slope positions. We used a value of 15°C for the reference temperature at which the CO_2 flux was standardized, as it corresponds to the mean of the observed temperatures. In a third stage, and in order to study the effect of the slope position, we calculated the time-integrated mean values for the five studied slope positions, for each of the three standardized CO_2 fluxes calculated before.

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To that end, we also used a GLS regression model, but with slope position as the unique explaining factor. This GLS model made it possible to achieve two by two comparisons (i.e. paired t-test) between slope positions.

4.3. Results

4.3.1. Controls on soil respiration

The observed soil temperatures range between 5.3 and 27°C and follow a normal distribution centered at 15.8°C (Figure 4.2). In contrast, the soil water content data has a lognormal distribution ($p < 0.001$), with a median value of 33.6% VWC (i.e. 76.7% WFPS). This data set offers a very broad range of soil moisture content values, from very dry (16.1 % VWC) to very wet (38.0% VWC) conditions. Figure 4.3 shows the temporal dynamics of the measured variables. The temporal evolution of soil respiration and soil temperature is very similar while trends of soil moisture and soil respiration are opposed (Figure 4.3). Note that the early spring of 2011 and the middle of the summer of 2012 both correspond to short and dry periods relative to the entire measurement period.

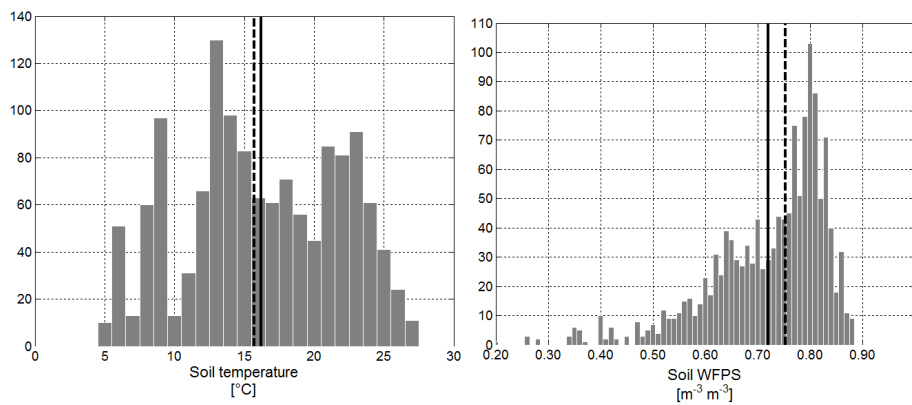


Figure 4.2. Frequency histograms of measured data for soil temperature and soil water-filled pore space (WFPS); plain lines represent mean values (in time and space) and dashed lines represent median values (in time and space).

Controls of surface respiration flux

The main relationships between the observed variables are summarized in Table 4.1, as a result of the regression analysis using Eq. 2. These results show that for dry conditions (below 57% WFPS or 25% VWC), the only significant explanatory variable is soil moisture (positive effect, $p < 0.001$), while labile OC and temperature are not significant ($p = 0.85$ and 0.34 , respectively). In contrast, under wet conditions (i.e. above 57% WFPS or 25% VWC) soil moisture has a negative effect on soil respiration, and both the effects of labile OC stock and soil temperature on soil respiration are positive and significant (Table 4.1). The model explains c. 50% ($R^2 = 47\%$) of the observed variability in CO_2 fluxes.

Table 4.1. Results of the statistical model explaining soil surface respiration fluxes observations (value of the model parameters and their significativity) for “dry” and “wet” soil water content ranges.

Intercept = $\ln(a)$	b	Q10	c
Dry conditions (data with water content < 25% VWC)			
-5.17 ± 1.61 **	N.S.	1.00 ± 0.00	1.60 ± 0.42 ***
Wet conditions (data with water content > 25% VWC)			
-0.32 ± 0.26 ^{N.S.}	0.42 ± 0.12 ***	Cat.1. 1.77 ± 0.18 ***	-1.35 ± 0.56 *
		Cat.2. 2.59 ± 0.13 ***	
		Cat.3. 3.42 ± 0.17 ***	

Model equation: $\ln(R_s) = \ln(a) + b \ln(\text{LOC}) + \ln(Q_{10}) \left(\frac{T-15}{10} \right) \text{WFPS. cat.} + c \ln(\text{WFPS})$

R_s is respiration flux (explained variable);

Model residuals follow a normal distribution ($p < 0.1$) and have also been tested for heteroskedasticity;

N.S. = not significant parameter;

WFPS = water content expressed here in terms of water-filled pore spaces (WFPS).

VWC = volumetric water content (with 25% VWC corresponding here to 57% WFPS).

Cat. = soil moisture categories: cat. 1. (57-68% WFPS or 25-30 % VWC), cat. 2. (68-80% WFPS or 25-30% VWC), cat. 3. (>80% WFPS or > 35% VWC).

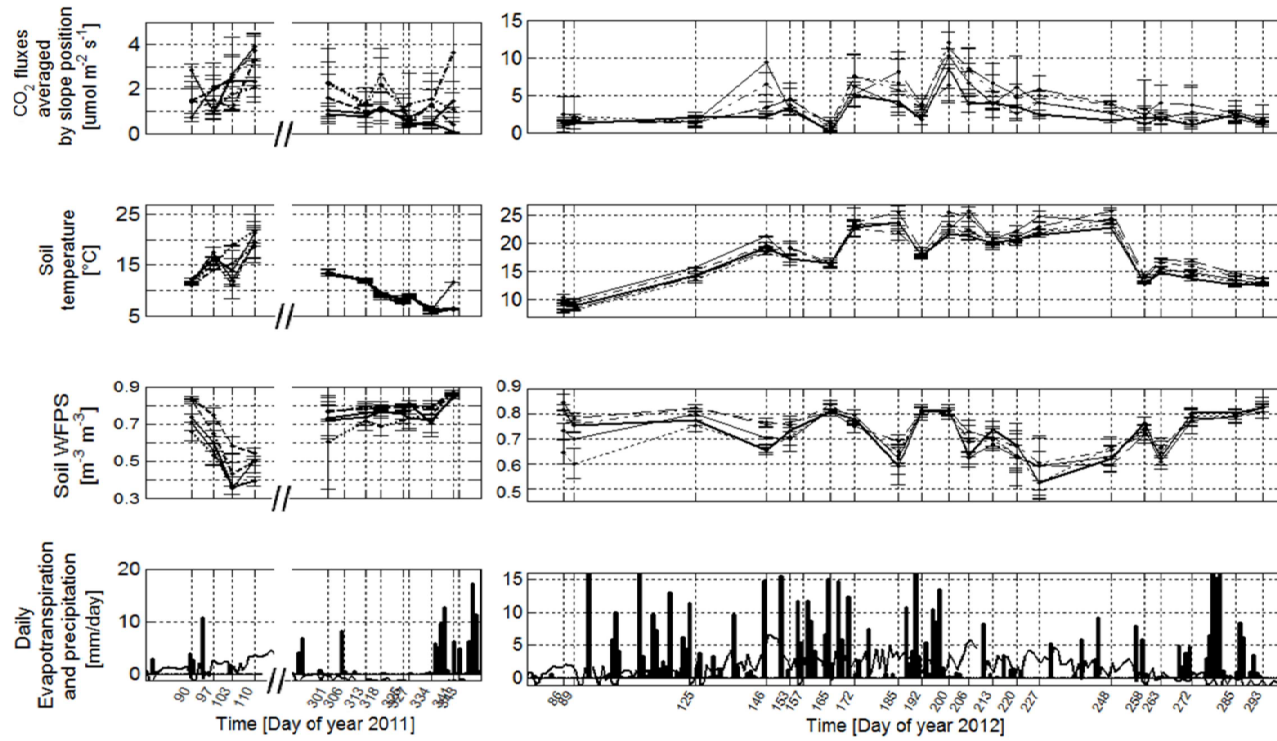


Figure 4.3. Temporal evolution of soil CO₂ fluxes, soil temperature, soil water-filled pore space (WFPS), daily evapotranspiration (continuous line) and precipitation during the measurement period (2011 to 2012). The values represent the average and standard deviation (error bars) for each of the 5 slope positions.

Controls of surface respiration flux

We will now explore the effect of the interactions between soil temperature and moisture on soil respiration in more detail. Figure 4.4 illustrates the synergetic effect of soil moisture and temperature on soil respiration by plotting a 3-D response surface. This indicates that the highest respiration rate averaged by slope position of each measurement date ($c.8 \mu\text{mol m}^{-2} \text{s}^{-1}$) occurs when both temperature and moisture content are the highest (Fig. 4.4).

The Q10 parameter represents a good indicator for the vulnerability of soil OC. Our results show that the temperature sensitivity, as reflected by the Q10 values (Figure 4.5), is dependent on other abiotic variables. More precisely, we observe that Q10 exponentially increases with water content (Fig.5). As reported above, there is no temperature effect ($p=0.85$) below 57% of WFPS, i.e. $Q_{10}=1$, while Q10 reached a value of up to 3.42 ± 0.19 above 80% of WFPS (Figure 4.5).

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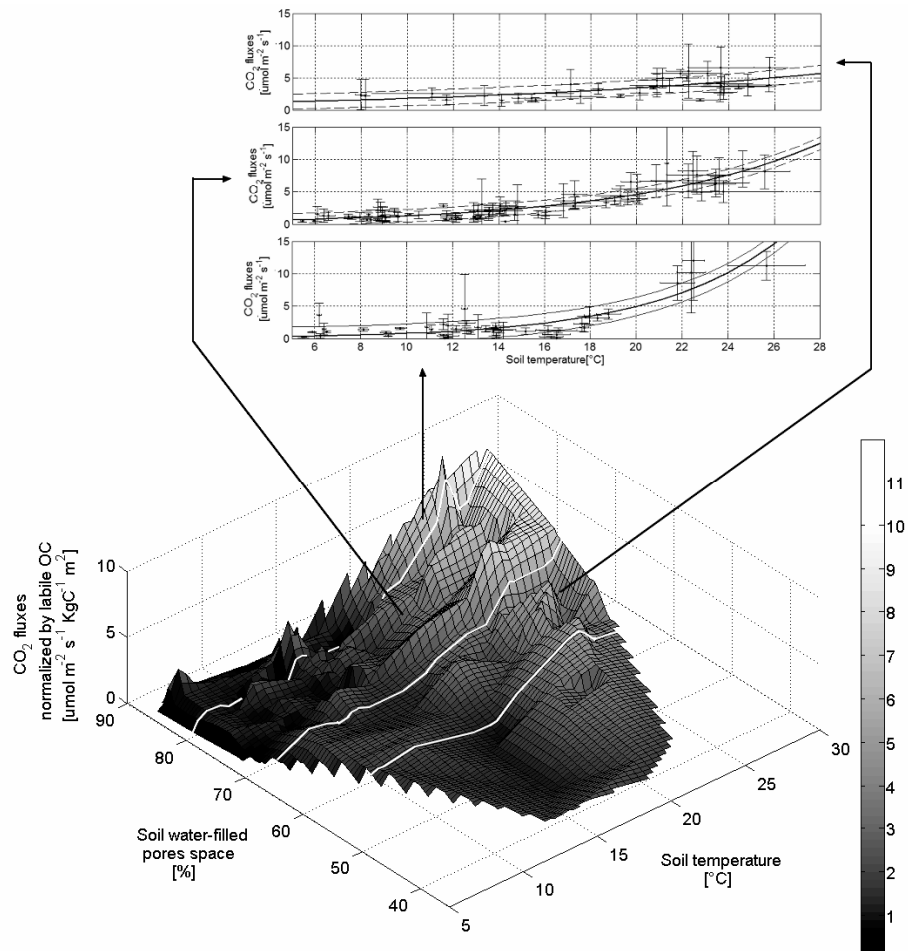


Figure 4.4. Respiration response surface (observed data interpolation) for the combined effect of soil WFPS (water-filled pore space) and soil temperature. 170 observation points were used here (34 dates x 5 slope positions). Errorbars indicate variability around the mean for each day at each slope position. Plain red lines indicate boundaries between WFPS categories (<57%, 57-68%, 68-80%, >80%). For each WFPS category, a Q10 model fit is shown through observed temperature and respiration data.

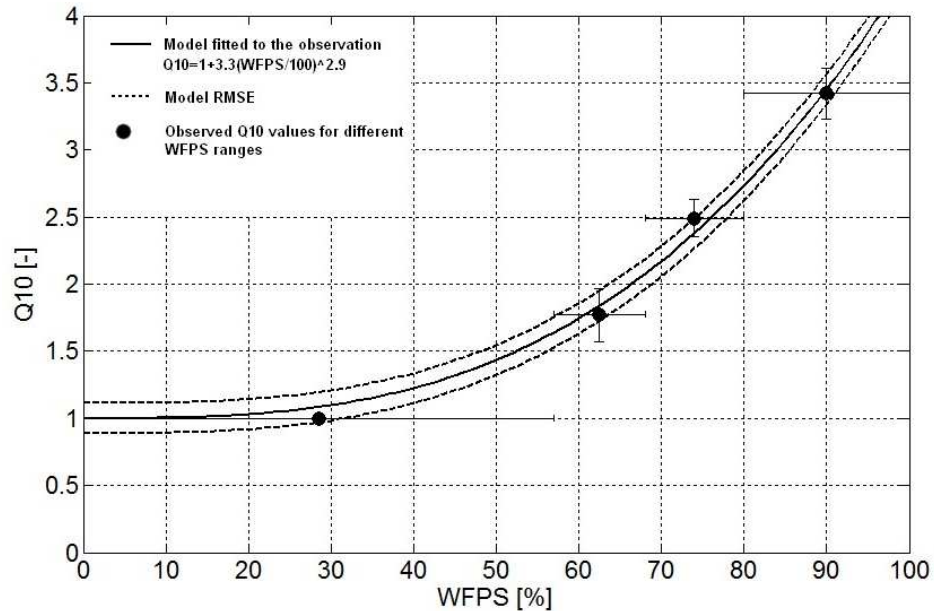


Figure 4.5. Temperature sensitivity (Q10 values) of soil respiration explained by water content in terms of Water Filled Pore spaces (WFPS) (points=measured data; plain lines=Q10 model; dashed lines= Q10 model Root Mean Square Error).

4.3.2. Spatial distribution of CO₂ fluxes along the hillslope

The soil respiration flux, as well as the VWC and labile OC stock, exhibit a strong spatial gradient along our hillslope (Fig. 4.6). When averaged over the period of observation, respiration rates are higher at the bottom of the slope than at the top. This pattern coincides with the hillslope variation in labile OC stock and VWC.

We found no evidence for systematic spatial differences in temperature along the hillslope (data not shown). Some temperature variations along the hillslope result from the different measurement times (measurement campaign of c.3 hours long). We removed this effect of different measurement times by

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standardizing the respiration data to a temperature of 15°C, using the above mentioned Q10 relationship (Table 4.1). The result is shown on Figure 4.6a.

The respiration increases from the summit to the footslope position (Fig.6 a). The respiration flux is c. 1.3 to 1.5 times higher at the footslope ($p \leq 0.05$), backslope ($p \leq 0.1$) and toeslope ($p \leq 0.05$) relative to the summit. When the respiration flux data are grouped into three topographical classes (“top” for summit and convex shoulder positions, “backslope” for the middle of the slope, and “bottom” for toeslope and footslope positions), the respiration flux at the top is significantly lower than the flux at the bottom ($p \leq 0.01$) and the backslope ($p \leq 0.05$).

The labile OC stock (integrated for a 1m soil profile) increases from the summit to the footslope (Figure 4.6 b) (Wiaux et al., 2014a - chapter 3 of this thesis). The labile OC stock is more than 2 times larger at the footslope than at the summit and the convex shoulder ($p \leq 0.05$), while there is also significantly more labile OC at the backslope than at the convex shoulder ($p \leq 0.1$). When the respiration rates are standardized for temperature and soil moisture (Eq. 4.1), and when only the effect of the labile OC is thus considered (Figure 4.6 b), the respiration rate increases from the summit to the footslope. We observe significant differences in temperature- and soil moisture-standardized respiration between the bottom (aggregated values for toeslope and footslope) and the top (aggregated values for summit and convex shoulder) classes ($p \leq 0.001$) as well as between the backslope and the top classes ($p \leq 0.05$).

The soil volumetric water content (VWC) is significantly different ($p \leq 0.001$) (Fig.6 c) at all slope positions, except for the toeslope and footslope. The spatial pattern of soil VWC is highly variable, with intermediate values at the summit. On average, VWC at the footslope is c. 8% higher than at the backslope, and 5% higher than at the summit and backslope positions. When the effects of temperature and labile OC stock are removed, and thus only the specific effect of soil VWC is considered (Fig.6 c), the mean respiration rate increases from the summit to the backslope, and then decreases at both the toeslope and the

Controls of surface respiration flux

footslope. These differences are significant ($p \leq 0.05$) at all slope positions, except for the backslope.

Compared to all controls on soil respiration, water content contributes c.40% at the footslope and the toeslope, and c. 50% at the other slope positions (ratio between the respiration rates specific to VWC and the sum of respiration rates specific to VWC and to labile OC, at each slope position).

The relative difference of respiration rates between downslope and top positions increases with temperature (Table 4.2). When considering a large temperature range – representative of seasonal variations on this study site – a large range of differences was observed between downslope and top positions (from 20% to 39%).

Table 4.2. CO₂ fluxes observations (Rs) standardized at different reference temperatures.

Reference temperature [°C]	CO ₂ fluxes [μmol m ⁻² s ⁻¹]									Relative difference of CO ₂ flux † [%]
	Downslope						Top			
				Backslope			(Summit & shoulder)			
	(footslope&toeslope)									
10	1.59	(±0.09)	a	1.74	(±0.13)	a	1.26	(±0.10)	b*	20
15	2.63	(±0.15)	a	2.69	(±0.21)	a	2.00	(±0.16)	b*	32
20	4.32	(±0.26)	a	4.17	(±0.37)	a	3.16	(±0.27)	b*	37
25	6.92	(±0.43)	a	6.54	(±0.62)	a	4.99	(±0.45)	b°	39
30	10.93	(±0.70)	a	10.38	(±0.99)	a	7.86	(±0.72)	b°	39

Mean values with different letters are significantly different from each other (Tukey–Kramer test, °:0.05< p <0.1; *: p <0.05).

† Downslope compared to top positions, using the formula: $100 * (Rs_Downslope - Rs_Top) / Rs_Top$.

All the data presented here are observations (not predictions). They only differ from each other on the temperature value used to standardize them. Number under brackets are standard deviations.

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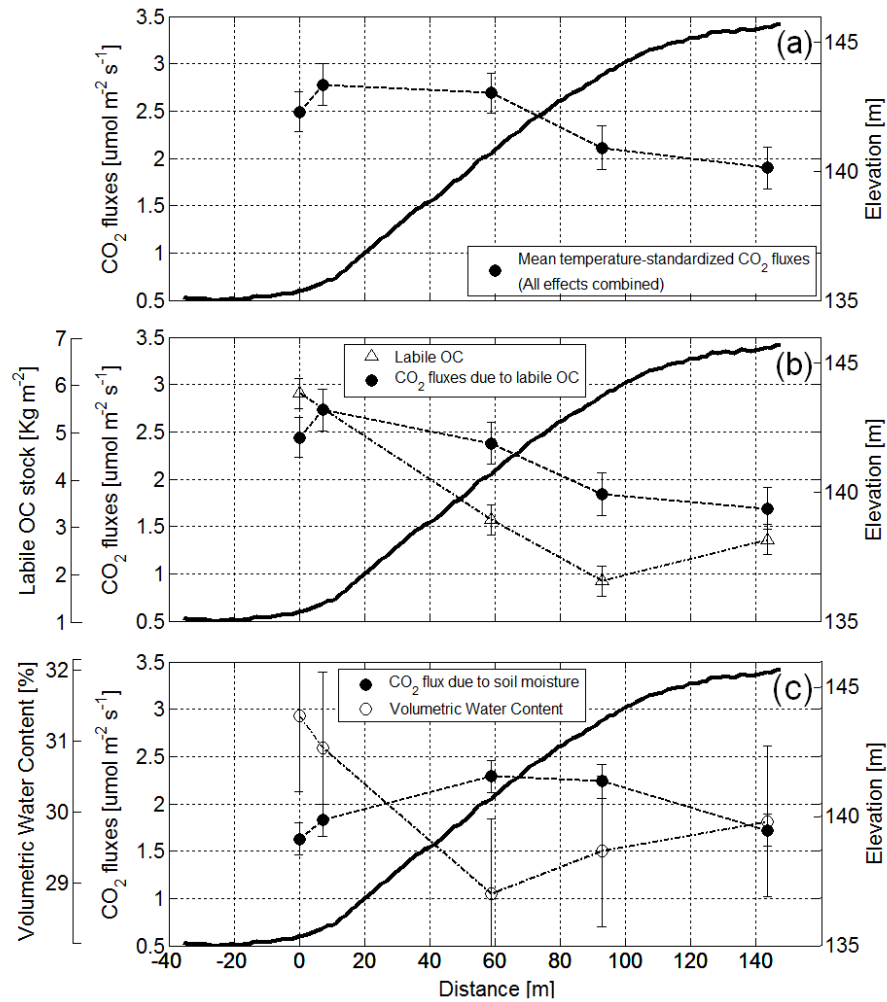


Figure 4.6. Effect of slope position on the different components of the soil surface respiration mean flux (plain dot): Temperature-standardized CO₂ fluxes (a); Temperature-and-WFPS-standardized CO₂ fluxes (b); Temperature-and-Labile OC-standardized CO₂ fluxes (c). Spatial distribution of controls on soil surface respiration are also illustrated: NaOCl-resistant OC stock (0-1m depth) (b); and Volumetric Water Content (VWC) (c). Plain bold line represents the hillslope profile. We found no evidence for systematic spatial differences in temperature along the hillslope (data not shown).

4.4. Discussion

4.4.1. Abiotic controls on soil respiration

Davidson et al. (1998) suggested that the statistical discrimination between the effects of temperature and water content on respiration is challenging due to their typically strong and negative correlation. However, our observations taken along the hillslope allowed us to disentangle the water and temperature effects. The abiotic conditions encountered in this study are characterized by a large water content gradient for a broad range of temperatures. The significantly lower water content at the backslope, relative to the other slope positions, can be explained by the fact that: (i) the 12% slope at the backslope induces a higher runoff ratio while more water may accumulate at the other slope positions (especially at the footslope); (ii) the presence of sand at c. 90 cm depth at the backslope results in the rapid drainage of water, while drainage is much slower at the other slope positions as sand only occurs below a depth of c.4 or c.5 meters (Wiaux et al., 2014a - chapter 3 of this thesis). In addition, the geomorphic processes (accelerated erosion due to agricultural land use, e.g. Van Oost et al., 2012) active on our site have led to a heterogeneous distribution of both OC quality and quantity along the hillslope (Wiaux et al., 2014a - chapter 3 of this thesis). Hence, the hillslope is an ideal site to achieve a robust statistical characterization of the main controls on soil respiration.

We found a positive relation between the labile OC stock (Wiaux et al., 2014a - chapter 3 of this thesis) and respiration. Nonetheless, no difference in labile OC stock for the upper 30 cm of the soil profile was observed along the hillslope (Wiaux et al., 2014a - chapter 3 of this thesis). In contrast to the surface layer, the labile OC stock for the upper 1m of the soil profile is heterogeneously distributed along the hillslope (Figure 4.6b). This spatial distribution of both OC quantity and quality has been thoroughly discussed by Wiaux et al. (2014a, chapter 3 of this thesis).

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Under dry conditions (i.e. <25% VWC), soil water content has a positive impact on soil respiration (Table 4.1) as: (i) soil water content increases the access of soil micro-organisms to their OC substrate, and (ii) soil micro-organisms need water for their own metabolic activities. When no other limiting conditions occur, this results in a global positive effect of soil moisture on soil respiration, as shown in this study and also suggested by Herbst et al. (2008). Under wet conditions (i.e. >25% VWC), the negative impact of water content on soil respiration (Table 4.1) is related to the lack of oxygen for the microbial community as a result of water filling soil pores. Water also acts as a diffusion barrier limiting CO₂ emission. In other words, the negative effect of VWC comes from its direct impact on decreasing soil gas diffusivity. However, this phenomenon goes beyond CO₂ production, and would need an adaptation of the regression model into an additive form (sum of production and diffusion terms) to explore it in more detail. Under dry conditions (i.e. <25% VWC), a positive impact was detected by the multiple regression model (Table 4.1). Our broad soil water content range (Figure 4.2) allows us to observe this bimodal relationship between soil water content and soil respiration (Table 4.1), with an optimal water content value at 25% VWC, as already suggested by (Bauer et al., 2012; Davidson et al., 1998; Perrin et al., 2004; Webster et al., 2008b).

It should be noted that the dry conditions (i.e. <25% VWC), under which an increase in soil water content stimulates OC mineralization (Table 4.1), are exceptional events (Figure 4.3). Given the temperate climate of our study site, and for the period considered, these conditions were rare and only occurred during the early spring of 2011 and in the middle of the summer of 2012 (representing c.15% of the observation period). Hence, most of the time, OC is protected (at least partly) from decomposition due to wet hydrological conditions (i.e. >25% VWC).

The commonly used exponential relation between soil respiration and soil temperature (Howard and Howard, 1993; Fang and Moncrieff, 2001; Perrin et al., 2004), as represented by the Q₁₀ model (Eq. 1), successfully simulates our observations (Table 1). Although a significant exponential effect of temperature

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was detected by the multiple regression model under wet conditions (i.e. >25% VWC), no temperature effect was observed under dry conditions (i.e. <25% VWC) (Table 4.1). The absence of temperature control under such dry conditions is consistent with other studies (e.g. Bauer et al., 2012; Herbst et al., 2008; Perrin et al., 2004). This can be explained by the fact that soil moisture is the limiting factor in such conditions and soil micro-organisms subjected to a permanent hydrological stress are not sensitive to an additional supply of thermal energy. Under wet conditions (i.e. >25% VWC), our results (Figure 4.4 and 5) also confirm the synergetic effect of soil water content and soil temperature on soil respiration (Akinremi et al., 1999; Davidson et al., 1998; Herbst et al., 2008; Howard and Howard, 1993; Perrin et al., 2004; Rochette et al., 1991). Finally, it should be noted that although the model is useful to identify the controlling factors, given its modest regression coefficient, we do not recommend using it in a predictive way.

4.4.2. Spatial distribution of CO₂ fluxes

Relative to the reference summit position, we observed that mean respiration fluxes (standardized at 15°C) were c. 1.3 times higher at the footslope, 1.5 times higher at the toeslope ($p \leq 0.05$) and c. 1.4 times higher at the backslope ($p \leq 0.1$). These observations are consistent with the results of Webster et al. (2008a; 2008b) in forest fields, who observed 1.6 higher median respiration fluxes at footslope and toeslope positions compared to the crest and convex shoulder positions. Our observations of soil water content and labile OC stocks (section 3) allow us to quantify the factors controlling this spatial pattern. The large and significant differences observed between the respiration fluxes of the different slope positions (Figure 4.6a) can be related to the heterogeneous distribution of soil water (Figure 4.6b) and the amount and the quality of soil OC (Figure 4.6c). However, we cannot exclude the possibility that other biogeochemical controls that are typically related to slope position such as the dissolved OC stock (Kalbitz et al., 2000), nutrients amount, microbial community heterogeneity (Stenrød et al., 2006), and factors impacting the

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accessibility of OC for soil micro-organisms such as soil aggregation (Doetterl et al., 2012) or soil type (Epron et al., 2006) play a role.

At the backslope, optimal conditions in terms of both OC substrate and soil moisture explain the high respiration flux which was observed; the average water content is close to the optimum value of c. 25% VWC, while intermediate values of labile OC stock are observed, relative to other slope positions. At this slope position, labile OC stock and VWC both contribute to the same extent on soil respiration (see section 3.2.).

At the top of the hillslope (i.e. summit and convex shoulder), the lower respiration fluxes which were observed relative to the other slope positions result from the combination of a high water content (relative to the optimum of 25% VWC) and a very low amount and proportion of labile OC. At this position, labile OC stock and VWC also both contribute to the same extent on soil respiration.

At the bottom of the slope, the CO₂ fluxes are controlled by the antagonistic effects of soil water and labile OC: the high water content at this site suppresses soil respiration, while the large amount of labile OC has the opposite effect and enhances respiration. Despite these antagonist effects, the contribution of labile OC is not completely balanced by the impact of VWC. This explains why respiration rates remain higher downslope relative to top-slope positions, despite the negative effect of VWC on soil respiration.

As a consequence, the hillslope studied here can be considered as a spatial succession of different ecosystems that are characterized by specific environmental conditions resulting in a gradient of OC persistence, as suggested by Schmidt et al. (2011). We suggest that these ecosystemic differences along our hillslope (c. 150 meters long with a 10 meter elevation difference) are sufficiently high to induce a strong spatial gradient in soil respiration with significant differences between slope positions of 30% to 50%.

4.4.3. Temperature sensitivity

The temperature sensitivity of soil OC decomposition (Q10) is a key parameter when assessing the present and future behavior of the OC stocks under changing climatic conditions (Luan and Liu, 2012). Our in situ measurements indicate that Q10 values are strongly dependent on soil water content (Figure 4.5). More precisely, Q10 exponentially increases with water-filled pore space (inversely proportional to oxygen availability) (Figure 4.5). This corroborates the kinetic and thermodynamic principles, which dictate that the temperature sensitivity of chemical reactions is inversely proportional to reaction rate (Arrhenius, 1889; Davidson and Janssens, 2006). This means that soil micro-organisms are more efficient in systems where OC is more difficult to degrade (e.g. because of lower oxygen conditions associated to high water contents). This effect likely results from the adaptation of soil micro-organisms to improve their mineralization efficiency in unfavorable environments, as suggested by Hartley and Ineson (2008). In a laboratory incubation experiment, Conant et al. (2008a) found no relationship between soil water and Q10. Luan et al. (2013) found a marginally significant effect of soil water on Q10. These laboratory-derived findings contrast with our observations and can be explained by two reasons. First, in contrast to the small range of water content tested in these studies, we were able to take advantage of a broad range of soil water values along the hillslope. Second, our study was carried out in situ, under real field conditions. Unlike manipulation experiments under laboratory conditions, the soil microbial community in our study was most likely well-adapted to the specific hydrological conditions of the different slope positions.

In the literature, a high spatial variation of Q10 has been observed across the landscape (Conant et al., 2011; Davidson et al., 1998; Luan et al., 2013; Luan and Liu, 2012; Xu et al., 2010), but has rarely been explained. In this study, given that the downslope positions are wetter (Fig.6) and the positive relation between Q10 and soil water (Figure 4.5), the large stock of soil OC stored in colluvial soils has a high temperature sensitivity. This explains why the CO₂ flux

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increase, in response to a temperature increase (Table 4.2), is much more pronounced at the downslope position.

4.4.4. Implications for soil OC persistence

Soil surface respiration rate can be interpreted as an indicator of soil OC persistence (e.g. Gregorich et al., 1994). The footslope of this study site is characterized by a large stock of OC and a large soil respiration flux. However, despite the fact that CO₂ fluxes at the footslope are higher than those at the other slope positions, the flux at the footslope is suppressed by the local soil hydrological conditions (section 3.2). Our regression model indicates that when soil water content is not accounted for, respiration rates at the footslope are c. 50% higher than at the summit position. However, the footslope respiration rates are only c. 30% higher due to the wetter conditions and stabilizing effect of soil water. This specific case-study provides evidence that OC persistence is not only related to its chemical composition or to its organo-mineral associations, but is controlled by the specific environmental conditions, i.e. soil moisture conditions (e.g. Kögel-Knabner et al. (2008); Schmidt et al. (2011)).

This has potential implications for the large amount of OC that is buried in colluvial soils as a result of agricultural land use and accelerated erosion (Montgomery, 2007). It is estimated that c. 16 to 21Pg of OC have been buried in colluvial deposits over the last c. 50 years (Van Oost et al. 2007). Although there are indications that this buried OC has stabilized over timescales of several decades (Van Oost et al., 2012), the long-term stability of these pools under future land use and/or climate disturbance remains uncertain. Soil water content, which controls the persistence of this buried OC, depends to a large extent on land use and meteorological conditions. The observations presented in this study strongly suggest that the OC found in colluvium (i.e. downslope positions) is particularly vulnerable to enhanced OC mineralization: (i) the OC stored in colluvial soils has been demonstrated to be easily decomposable by soil micro-organisms from a chemical point of view as it has a higher OC quality (*sensu* Mikutta et al. (2005); Siregar et al. (2005)) than non-colluvial soils

(Wiaux et al., 2014a - chapter 3 of this thesis); (ii) at this position, OC quality is the main factor controlling respiration and is more important than water content; and (iii) at this position, colluvial OC has a higher temperature sensitivity (Figure 4.5). This study confirms that colluvial deposits constitute an important stock of OC, where buried OC has been (at least partially) preserved from mineralization. However, our results strongly suggest that this OC stock is 20% to 40% more sensitive to temperature changes than in non-eroded slope positions. Changes in hydrological conditions or temperature along the hillslope related to environmental change are therefore a concern as these could potentially enhance the mineralization of the previously buried OC in colluvial soils (e.g. Chaopricha and Marín-Spiotta, 2014; Van Oost et al., 2012).

4.5. Conclusion

Our experimental setup along an eroding hillslope provided a very broad range of soil moisture, temperature and OC quality, which allowed us to identify their effect on soil respiration. These factors vary spatially along the hillslope and their effects on soil respiration depend largely on the hydrological condition. When averaged over the period of observation, we observe higher respiration rates (c. 30%) at the bottom of the slope than at the top. This pattern coincides with spatial gradients in labile OC stock and water content. The large stock of labile OC found at the bottom of the slope results in enhanced soil respiration. However, this effect is substantially suppressed by the wetter soil conditions at the same slope position.

Our in situ measurements also indicate that Q10 values are strongly dependent on soil water content. The large stock of soil OC stored in colluvial soils has a high temperature sensitivity, relative to non-depositional profiles, due to the fact that the downslope depositional positions are wetter and the existence of a positive relation between Q10 and soil water content. When considering the large stock of labile OC, its high temperature sensitivity and the high water contents that are needed to stabilize OC, we conclude that the OC stored in colluvial soils is particularly vulnerable to OC mineralization. Drier conditions or

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increases in mean temperature could potentially lead to an enhanced mineralization of this depositional OC stock. Given the large amount of OC that has been buried as a result of agricultural erosion during the last decades (e.g. Doetterl et al. 2012), the long-term stability of this pool under future land use and/or climate disturbance is an area of concern.

5. The gradient method for soil CO₂ fluxes calculation

5.1. Introduction

Current predictions of the exchange of C between the soil and the atmosphere are associated with large uncertainties (Houghton et al., 2003; Peters et al., 2010).

Infra-red gas analyzer (IRGA) linked to automated closed dynamic survey chambers (e.g. Davidson et al., 2002) are often used to perform punctual records of surface CO₂ emissions, while surface high frequency measurements are possible but quite expensive. This may lead to bias if instantaneous measurements are extended to a larger time-scale, in particular since measurement campaigns are often carried out during emissions peaks (Turcu et al., 2005).

Another source of uncertainty is the lack of understanding of the role of buried OC on soil C emissions (e.g. Van Oost et al., 2012; Wang et al., 2014; Wiaux et al., 2014). Rumpel and Kögel-Knabner (2011) highlighted that deep soil OC is highly processed, and showed the need for quantitative information about C fluxes coming from deep soil horizons. CO₂ fluxes within the soil profile can be assessed by means of the gradient-based method (Davidson et al., 2006; Gaudinski et al., 2000; Maier and Schack-Kirchner, 2014; Pingintha et al., 2010; Tang et al., 2003; Turcu et al., 2005).

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Several studies have reported good correlations between surface soil CO₂ fluxes obtained by means of the IRGA chamber method and the gradient-based method (Pingintha et al., 2010; Tang et al., 2003; Turcu et al., 2005). With the gradient-based method, soil CO₂ concentration is measured at different depths within the profile and is then used to define a concentration gradient. Subsequently, a CO₂ flux is calculated using Fick's first law (e.g. Maier and Schack-Kirchner, 2014). CO₂ concentration in soils can be measured accurately, precisely and at a very high frequency by means of the non-dispersive infra-red (NDIR) technology (e.g. CARBOCAP® CO₂ probes, Young et al., 2009). Notwithstanding the gradient-based method is used in an increasing number of studies, estimates of CO₂ fluxes remain subjected to large uncertainties and challenging improvements (Maier and Schack-Kirchner, 2014).

The main sources of uncertainty in the gradient based method are related to the following issues. First, the selection of the empirical model to calculate the relative gas diffusion coefficient (e.g. Millington and Quirk, 1961; Moldrup et al., 1997, 1999, 2000; Pingintha et al., 2010; Tang et al., 2003) is always done specifically to each soil type, preventing from finding a universal best diffusion model (Maier and Schack-Kirchner, 2014). Second, the detailed knowledge of water content within the soil profile is often lacking, while the soil water content profile has been identified as a key factor in the calculation of gas diffusivity (Maier and Schack-Kirchner, 2014; Turcu et al., 2005). Third, replicated samples for CO₂ concentration measurements are often not available, both limiting the footprint area of this technique relative to the IRGA chamber method and assuming an unrealistic horizontal homogeneity of CO₂ concentration (Maier and Schack-Kirchner, 2014). Fourth, the vertical profiles of soil CO₂ concentrations can be fitted by an analytical differentiable and continuous function, but currently used functions fail either to correctly represent the observation or to provide accurate estimation of the surface CO₂ flux (Maier and Schack-Kirchner, 2014). Fifth, current applications of this technique focus on surface soil layers, with the deepest CO₂ concentration measurements located at too shallow depths (e.g. 12 cm depth in Pingintha et al., 2010; 16 cm depth in Tang et al., 2003 and 22 cm depth in Turcu et al.,

2005). Sixth, the measurement range of currently available probes is limited and not always adapted to in-situ measurements (Pingintha et al., 2010; Young et al., 2009). There is therefore considerable scope to increase the performance of gradient-based CO₂ flux assessments (Maier and Schack-Kirchner, 2014).

In this study, we aim to improve the use of the gradient-based method for assessing CO₂ fluxes in the soil-atmosphere continuum. More specifically, through the evaluation of the method for two contrasted soil profiles in the Belgian loess belt, we bring new insights in the use of the gradient-based method by (i) suggesting a new analytical function to fit the concentration profile, and (ii) selecting a unique best diffusion model suitable for the two contrasted soil types.

5.2. Material and methods

5.2.1. Two contrasted soil profiles

The study site and the overall experimental set-up have been described in details in chapter 2.

We selected 2 measurement stations along the hillslope: one at the summit and one at the footslope position. The studied soils are both silt-loamy soils, but they differ in their profile development. The toposequence consists of a Dystric Luvisol at the summit while a Colluvic Regosol is observed in the depositional area at the footslope (WRB, 2014). At each of these two contrasted soil profiles, a thorough characterization of physical and hydrodynamic properties was performed. Both disturbed and undisturbed soil cores were collected along the soil profile from 5 to 95 cm depth, with 10 cm depth intervals. 100 cm³ metal cylinders were used to collect undisturbed soil cores.

Disturbed samples, used for texture analysis, were firstly passed through a 2 mm sieve and then dispersed using a Na₂CO₃ and sodium hexametaphosphate solution. Granulometric analyses for clays were then performed according to

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the Robinson pipette method (AFNOR-NF X 31-107 norm) with a Texsol24B (LCA Instruments, France) sedimentation automate. For clay content, the analytical error was 0.5 %. A unique value was used for each depth.

The total porosity ($\emptyset$) was measured in the laboratory by weighting 100 cm³ undisturbed soil cores both at saturation and after oven drying at 105°C during 48h. The total porosity ($\emptyset$) was then deduced from the mass of water needed to fill sample pores. The air-filled porosity (ϵ) was calculated as the difference between $\emptyset$ and VWC (section 5.2.2 and 5.2.3). Average and standard deviation values were calculated on triplicate samples for each depth.

Soil water retention (SWR) curves were characterized using undisturbed soil cores at 10, 25, 35, 50, 70 and 95 cm depth, with 3 replicates at each depth. ϵ_{100} and b parameters were obtained by fitting the Campbell (1974) model of SWR curve to the SWR observations (Moldrup et al. 2000).

5.2.2. Building a new analytical function to fit CO₂ concentration profiles

The flux of CO₂ diffused from the soil can be calculated using Fick's first law of diffusion (Eq. 5.1).

$$F_{CO_2} = -D_s \frac{\partial CO_2}{\partial z} \quad (\text{Eq. 5.1})$$

where F_{CO_2} is the CO₂ flux [$\mu\text{mol m}^{-2} \text{s}^{-1}$], D_s the diffusivity of CO₂ in soil [$\text{m}^2 \text{s}^{-1}$], CO₂ the soil CO₂ concentration [$\mu\text{mol m}^{-3}$], and $\frac{\partial CO_2}{\partial z}$ the vertical soil CO₂ gradient.

In order to calculate the vertical soil CO₂ gradient, we established a model describing the vertical soil CO₂ concentration profile. Notwithstanding many authors used a simple decreasing exponential model (e.g. Gaudinski et al., 2000; Davidson et al., 2006), others suggest more complex models, allowing to represent more complex soil CO₂ profiles induced by diffusion barriers within

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the soil (Johnson et al., 1994). We used a double sigmoidal equation (Eq. 5.2), which allows accounting for some curve concavity variations. The physical meaning of the inflection point in the CO₂ profile model is that CO₂ can accumulate at a given depth due to a gas diffusion barrier associated with high VWC and/or to locally compacted soil layers.

$$CO_2(z) = 0.04 + A \left(\left(\frac{1}{1+e^{-\gamma_1 z}} \right) + \left(\frac{1}{1+e^{-\gamma_2(z-d)}} \right) - \left(\frac{1}{2} + \frac{1}{1+e^{\gamma_2 d}} \right) \right) \quad (\text{Eq. 5.2})$$

where z is soil depth [cm], d is the soil depth [cm] at which the sharpness of the curve changes due to a diffusion barrier, γ_1 and γ_2 [cm⁻¹] are fitted parameters which characterize the sharpness of the curve, respectively above and below the soil depth d , and A [%] is a reference value used to define the fitted asymptotic value of the CO₂ concentration at infinite depth $CO_{2,\infty}$ [%], defined by Eq. 5.3:

$$CO_{2,\infty} = 0.04 + A \left(1.5 - \frac{1}{1+e^{\gamma_2 d}} \right) \quad (\text{Eq. 5.3})$$

Eq. 5.2 simply corresponds to the sum of two sigmoidal curves which differ from each other in both the sharpness of the curve and the departure points on the soil depth (z) axis. The last term is a constant which corresponds to the zero of these sigmoidal equations, and is subtracted to make the curve to fit with the atmospheric CO₂ concentration (0.04 %).

The fitting parameters A , d , γ_1 and γ_2 were evaluated for each profile observation in time using a trust-region-reflective optimization (inversion) algorithm in Matlab ©. The derivative of this function (Eq. 5.2), calculated analytically, provided the CO₂ gradient ($\frac{\partial CO_2}{\partial z}$) used in Eq.1.

5.2.3. Choose of a unique diffusion model

The diffusivity of CO₂ in soil (defined as D_s in Eq. 5.1) is a function of the diffusivity of CO₂ in free air (D_o) and of the gas tortuosity factor (ξ) (Eq. 5.4).

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$$D_s = \xi D_o \quad (\text{Eq. 5.4})$$

Here D_o is a reference diffusivity value varying with temperature (T) and pressure. Here, we calculated D_o according to Eq. 5.5 (e.g. Davidson et al., 2006).

$$D_o = 1.47 \cdot 10^{-5} \left(\frac{T+273}{273} \right)^{1.75} \quad (\text{Eq. 5.5})$$

ξ depends on soil physical and hydrological properties, and has been described by several empirical models. Some of them have already been applied to CO₂ diffusion in soils (e.g. Davidson et al., 2006; Pingintha et al., 2010; Tang et al., 2003) but were always specific to a given soil type (Maier and Schack-Kirchner, 2014). In this study, we compared four different models to calculate ξ for the two contrasted soil types at the same time, as described in Eqs. 6 to 9.

$$\xi = \frac{\varepsilon^{10/3}}{\emptyset^2} \quad (\text{Millington and Quirk, 1961}) \quad (\text{Eq. 5.6})$$

$$\xi = 0.67 \varepsilon \left(\frac{\varepsilon}{\emptyset} \right)^3 \quad (\text{Moldrup et al. 1997}) \quad (\text{Eq. 5.7})$$

$$\xi = \emptyset^2 \left(\frac{\varepsilon}{\emptyset} \right)^{2.9S} \quad (\text{Moldrup et al. 1999}) \quad (\text{Eq. 5.8})$$

$$\xi = (2\varepsilon_{100}^3 + 0.04\varepsilon_{100}) \left(\frac{\varepsilon}{\varepsilon_{100}} \right)^{2+3/b} \quad (\text{Moldrup et al. 2000}) \quad (\text{Eq. 5.9})$$

where ε [m³ m⁻³] is the soil air-filled porosity, $\emptyset$ [m³ m⁻³] is the total soil porosity, S is the percentage of mineral soil with particle size > 2 μ m (= 100 - clay content), b [-] is the slope of the Campbell (1974) soil water retention curve model between -100 and -500 cm H₂O water suction, and ε_{100} [m³ m⁻³] is the soil air-filled porosity at a soil water potential of -100 cm H₂O.

In contrast to other studies (e.g. Pingintha et al., 2010; Turcu et al., 2005), soil CO₂ diffusivity was not aggregated for the entire soil profile or for an entire soil layer, but its vertical distribution was accounted for. All the above-mentioned parameters ($\emptyset, \varepsilon, S, b, \varepsilon_{100}$) were estimated at different depths along the soil

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profiles (section 2.6), and then interpolated to generate continuous profiles, as for VWC, temperature. Then, Eqs. 5.6-5.9 were inserted in Eq. 5.1, and Eq. 5.1 was numerically evaluated using the Euler integration method and adopting a depth increment of 0.1 cm. The surface CO₂ flux obtained with the gradient-based method was considered as being the top of the calculated CO₂ flux profile using Eq. 5.1.

5.2.4. Precise and adapted measurements of CO₂ concentrations

We measured soil surface CO₂ fluxes by means of a portable infra-red gas analyzer with an automated closed dynamic chamber (LI-8100A system, LI-COR, United-States), following Davidson et al. (2002).

We also measured soil CO₂ concentrations by means of specific designed soil CO₂ probes. The CO₂ sensor in the probe is based on the CARBOCAP® Single-Beam Dual Wavelength non-dispersive infra-red (NDIR) technology (GMM221, Vaisala corp., Vantaa, Finland). Analytical precision is 1.5% of the measurement range (e.g. 1.5% of 5 000 ppm) added to 2% of the observed value (e.g. 2% of 3 300 ppm).

The sampling head of the CO₂ probe is a cylinder of 18.5 mm diameter and 40 mm long, covered with a PTFE (polytetrafluoroethylene) membrane, enabling gas exchange and protection against water infiltration. Since the GMM221 sensors were not designed for wet soil conditions, the sensors were encapsulated into an additional perforated PVC tube, providing an additional protection against water (Figure 5.1). This tubing method is an adaptation of the technique presented by Young et al. (2009). These tubes were inserted vertically into the soil, after augering holes with a diameter that equals the diameter of the PVC tubes. Two rubber stoppers, one at 155 mm from the tube head, and another at the top of the tube, prevented atmospheric air from penetrating into the gas sampling volume. Petroleum jelly on these two rubber stoppers ensured a perfect air- and water-tightness (tested in laboratory). A

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nylon membrane was used to avoid soil particles entering the perforated tube and to limit further water infiltration.

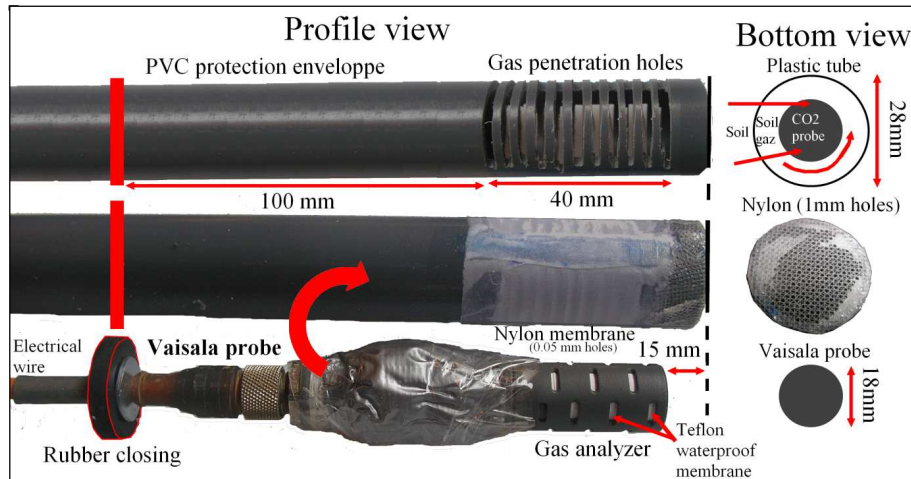


Figure 5.1. Description of the probes used for CO₂ concentration measurements inside the soil.

Each CO₂ probe consumes less than 2.5W. Hence, we can reasonably assume that the alteration of the local soil microclimate due to soil heating is likely to be insignificant. However, in order to minimize the effect of soil heating due to power consumption around the probes, we used an electrical relay to switch on the probes only 5 minutes before each measurement and to switch it off directly after each measurement. In addition, we isolated the probe with synthetic foam.

To optimize the quality of the soil concentration data time-series, observations corresponding to battery voltage lower than 11.5 V were removed. Soil profile CO₂ concentrations measurements were a posteriori corrected for temperature variations using the empirical formulas described by Tang et al. (2003). This allowed removing the impact of temperature on the CO₂ reading of the CO₂ probe, since the CARBOCAP® technology is temperature dependent. Probe specific parameters values for these correction formulas were provided by the probe manufacturer (Vaisala corp., Vantaa, Finland).

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Vaisala CO₂ probe concentrations ranges were adapted to each soil depth and to each slope position. This allowed catching the entire expected range of observations without impacting the quality of observation in terms of precision. At the summit position, measurement ranged between 0-2 % at 12, 25, 45 cm depth and between 0-5 % at 85cm depth. At the footslope position, measurement ranged between 0-5 % at 12 cm depth, between 0-10 % at 25 and 45 cm depth and between 0-20 % at 85cm depth.

5.2.5. Replicated measurements of CO₂ at each depth

At each of the 2 slope positions, we measured soil CO₂ concentrations profiles at 4 soil depths with 3 replicates on each depth (Figure 2.8.8). This allowed catching the spatial variability of CO₂ concentrations at the different depths (Maier and Schack-Kirchner, 2014), extending the measurement footprint to the same area (i.e. 5 m²) than the IRGA chamber network located at the soil surface (Figure 2.8.8). Triplicate CO₂ concentrations data were averaged, providing unique values for each depth, representative of the entire slope position. Continuous CO₂ concentrations profiles were generated by fitting a decreasing double sigmoidal model to the observations (section 2.2).

We measured soil surface CO₂ flux, at each of the 2 slope positions, on 6 collars. The collars had a diameter of 20 cm diameter and were installed at the soil surface inside an area of 5 meters long and 1 meter width (Figure 2.8.8). The measurements on 6 collars allowed quantifying the small-scale spatial variability of soil surface CO₂ flux. Each measurement was repeated two times. Weekly soil surface CO₂ fluxes measurements began during the spring 2010 and stopped during early winter 2013. At each slope position and at each measurement date, we calculated mean values of soil surface CO₂ fluxes on the 12 measurements (6 spatially replicated collars, 2 time-replicates).

To obtain an equilibrated soil environment around the soil concentration probe, we started measurements 1 month after the probes installation. Hourly time-series measurements along soil profiles were achieved from 7 June 2012

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until 14 December 2012, and from 9 May 2013 until 22 November 2013. We matched both profile and surface data in time, selecting data recorded on the same day and displaying a maximum time-lapse of 30 minutes between profile and surface measurements. This resulted in a restricted dataset of 16 CO₂ data (for the two slope positions). This dataset allowed a direct comparison between surface IRGA flux measurements and gradient-based calculated surface fluxes.

The measurement plots were covered with a synthetic permeable geotextile during the complete measurement period. This avoided vegetation growth and any autotrophic contribution to the soil respiration.

5.2.5. Detailed knowledge of water content and temperature

For soil VWC profiles, at each of the 2 slope positions, 18 measurements were collected (6 soil depths, 3 replicates). Sampling depths for VWC were 10, 25, 35, 50, 70 and 95 cm. This allowed a detailed knowledge of water content within the soil profile, identified as a key factor in the calculation of gas diffusivity (Maier and Schack-Kirchner, 2014; Turcu et al., 2005).

Soil volumetric water content (VWC) was monitored using Time Domain Reflectometry (TDR) probes. Topp's equation (Topp et al., 1980) was used to determine VWC, from the apparent dielectric constant measured by TDR probes. The parameters of the Topp equation were those identified by Beff et al. (2013). They calibrated Topp's equation for an experimental field in the close vicinity of our field, using the method of Heimovaara (1993) and following the protocol described by Garré et al. (2008). The probes were connected to a TDR multiplexer (CampbellSDMX50, Campbell Scientific Lt., UK) controlled by an automatic data logger (CR10X, Campbell Scientific Lt., UK). TDR signals were generated and automatically analyzed by means of a TDR100 system (Campbell Scientific Lt., UK).

Triplicate VWC were averaged for each depth. Continuous soil temperature and VWC profiles were calculated using a linear interpolation between the depth

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specific values. Surface values were not extrapolated, and were considered as being equal to the closest observations in the profiles (i.e. at 10 cm depth).

For temperature, 4 soil depths (10, 25, 45, 85 cm) without replicates were measured, reasonably assuming an horizontal homogeneity of soil temperature contrary to the other measured variables (Figure 2.8.8). Soil temperature was monitored using a thermistor probe (Therm107, Campbell Scientific Lt., UK). Analytical precision is 0.4°C.

5.3. Results

5.3.1. Shape of CO₂ profiles

CO₂ concentrations increase with depth, ranging from the atmospheric value of 0.04 % until 2 order of magnitude higher concentrations at 100 cm depth (CO_{2,∞}, Table 5.1)(Figure 5.2). CO_{2,∞} are c. 4 times higher at the footslope position than at the summit position, ranging from c. 1.22 to 3.44 % at the summit position and from c. 4.54 to 8.76 % at the footslope position (Table 5.1). Standard deviations around averaged values of observed CO₂ concentrations are relative low.

Both Figure 5.2 and Table 5.1 show that the double sigmoidal equation fits well the soil CO₂ concentration observations along the two studied vertical soil profiles. Regression coefficients range between 97 to 100% depending on the date and on the slope position. As illustrated in Figure 5.2, an inflection can be observed at precise depths along the soil profile. The position of the inflection, as assessed by the *d* values (Table 5.1), situates between 42 and 80 cm depth. The inflection point is more pronounced at the footslope position as compared to the summit position (Figure 5.2).

The single exponential model (dotted lines, Figure 5.2) fits the CO₂ concentration profile, if soil measurements below c. 42 cm are ignored. As illustrated in Figure 5.2, the slope of the concentration profile nearby the surface varies with the selected model.

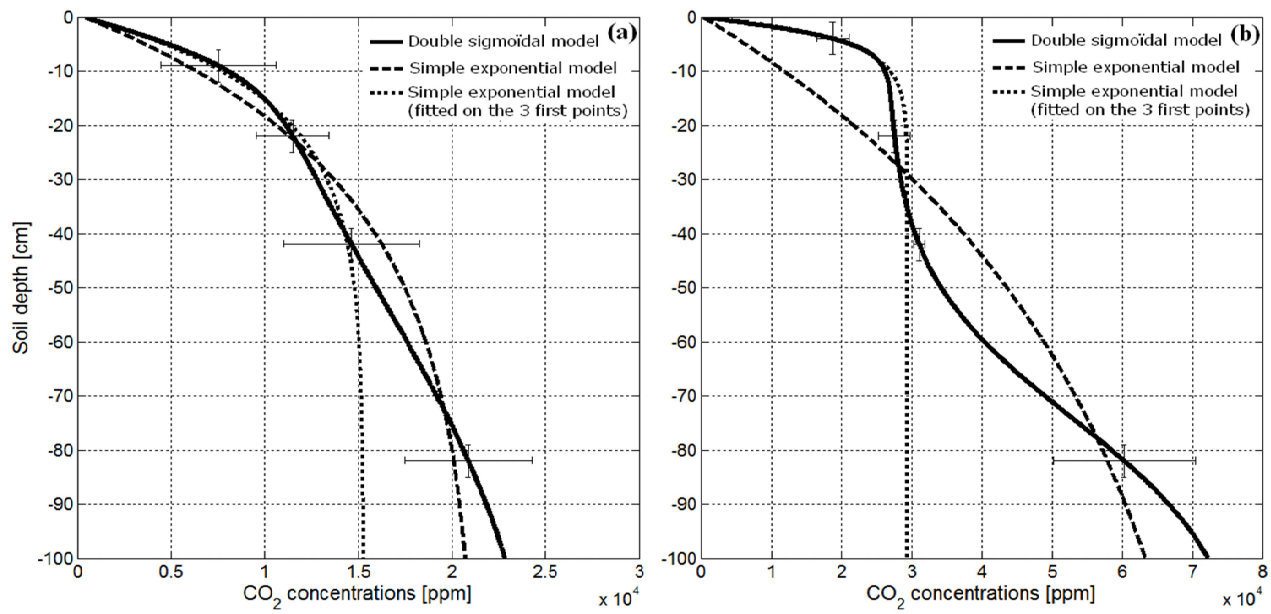


Figure 5.2. Example of CO₂ concentration profiles at DOY 196 in 2013 (dots=observation; continuous curve=fitted model) at the summit of the hillslope (a) and at the footslope colluvium (b). Errorbars illustrate standard deviation on triplicates.

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Table. 5.1. Fitted parameters values of CO₂ concentration profiles and regression coefficient of the fitted model at different dates at the two studied slope positions.

Slope Position	DOY #	A [%]	$CO_{2,\infty}$ [%]	γ_1 [-]	d [cm]	γ_2 [-]	R ²
Summit	227*	1.32	1.98	0.21	43	0.08	100
Summit	154	0.80	1.22	0.38	42	0.09	100
Summit	158	1.11	1.53	0.46	43	0.04	100
Summit	189	2.64	2.82	0.19	42	0.02	100
Summit	196	1.85	2.54	0.19	53	0.04	100
Summit	227	1.83	2.77	0.13	68	0.07	100
Summit	242	2.21	3.28	0.13	80	0.04	100
Summit	247	2.33	3.44	0.10	80	0.04	99
Summit	304	1.56	2.38	0.09	80	0.07	99
Summit	317	1.23	1.84	0.08	80	0.04	100
Footslope	183	4.79	7.23	0.80	80	0.09	99
Footslope	189	5.88	8.76	0.73	80	0.05	97
Footslope	196	5.26	7.9	0.43	74	0.07	100
Footslope	242	5.51	8.27	0.40	73	0.07	100
Footslope	247	5.19	7.82	0.34	64	0.11	100
Footslope	304	3.55	5.37	0.20	78	0.13	100
Footslope	317	3.00	4.54	0.13	80	0.11	99

DOY=Day of year;

Data were collected in 2013, except * in 2012.

% = volumetricpercentage= 10⁻⁴ ppmv

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5.3.2. Soil physical and hydrological properties

The soil physical properties of the two selected slope positions are very different (Figure 5.3, Table 5.2).

The soil porosity ranges from 34 to 43% at the footslope, and from 39 to 48% at the summit position (Figure 5.3b). Porosity values for the two slope positions are very similar, from 0 to c. 40 cm depth, and from 70 to 100 cm depth. However, they are very different from 40 to 70 cm. Within this intermediate soil layer, porosity increases at the summit position and decreases at the footslope position (Figure 5.3b).

The clay content ranges from c. 16 to 23% at the footslope position, and from c. 18 to 22 % at the summit position (Figure 5.3a). As compared to the summit position, the footslope exhibits a lower clay content until c. 50 cm depth, a higher clay content at c. 65 cm depth, and again a lower content at c. 95 cm depth (Figure 5.3a).

The b values of the SWR curve and the ϵ_{100} value are given in Table 5.2. ϵ_{100} is quite constant all along the soil profile, but is c. 2 times higher at the summit position as compared to the footslope position (Table 5.2). The b values at 10cm depth are quite similar for the two slope positions, but differ more strongly deeper in the soil profile (Table 5.2).

Figure 5.4 illustrates the VWC profiles for a given date (i.e. 15 July 2013). We observe that VWC nearly equals the porosity at some locations in the soil profile. Figure 5.4 also illustrates that, for this given date, the VWC profiles at the two slope positions strongly differ from each other. In this example, the VWC is very homogeneously distributed in depth at the footslope position. In contrast, at the summit position, VWC is strongly depth dependent (Figure 5.4a).

The space-time dynamics of soil volumetric water content (VWC, Figure 5.5) differ completely between the summit and the footslope. At the footslope, soil

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VWC values remained inside a narrow interval (36 to 39%) all along the soil profile during the considered period. At the summit, soil VWC varies from 23 to 34% in the plow layer (0-30cm depth) and then increases by an absolute value of 15 to 5% (respectively) in the rest of the soil profile. The soil at the summit position is the wettest during the early spring and the late autumn and driest in the summer. At the footslope soil VWC reaches the saturation level in the early summer after an important rainfall event and then slowly decreases until the early autumn and reaches saturation again in the late autumn.

Figure 5.6 illustrates that, on a given date, soil CO₂ diffusivity (exemple calculated with the model of Moldrup et al., 2000) is heterogeneously distributed within the profile. At the summit position, diffusivity values tend to zero at a depth c. 35 and c. 70 cm depth. At the footslope position, diffusivity values tend to zero from c. 40 to 50 cm depth. At these two slope positions, the diffusivity is the highest within the soil surface layer (0-30cm depth).

Figure 5.6 also shows the propagated error on soil CO₂ diffusivity, calculated as the sum of the measured errors on each explaining variables multiplied by the absolute values of the derivatives of the diffusivity equation the for these variables. This uncertainty around soil CO₂ diffusivity is the most important within the soil surface layer (0-30 cm depth), and can especially be important at the footslope position.

For the footslope position, we cannot statically discriminate the calculated diffusivity values from zero. The diffusivity profiles differ more than one order of magnitude between slope positions. In this example, at the footslope position, the diffusivity reaches c. $7.6 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ while at the summit it can reach c. $5.7 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

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Table 5.2. Soil water retention (SWR) parameters of the Campbell (1974) model at different depths along the summit and footslope profiles. For each depth and each slope position, one unique SWR curve was fitted to the averaged suction and water content data.

Depth [cm]	10	25	35	50	70	95
Summit						
$\epsilon_{100}[\text{cm}^3 \text{ cm}^{-3}]$	0.075	0.048	0.072	0.074	0.066	0.066
$b [-]$	8.35	5.48	11.83	5.75	5.82	5.82
Footslope						
$\epsilon_{100}[\text{cm}^3 \text{ cm}^{-3}]$	0.030	0.030	0.033	0.040	NI	0.031
$b [-]$	8.98	4.81	7.76	8.74	NI	8.74

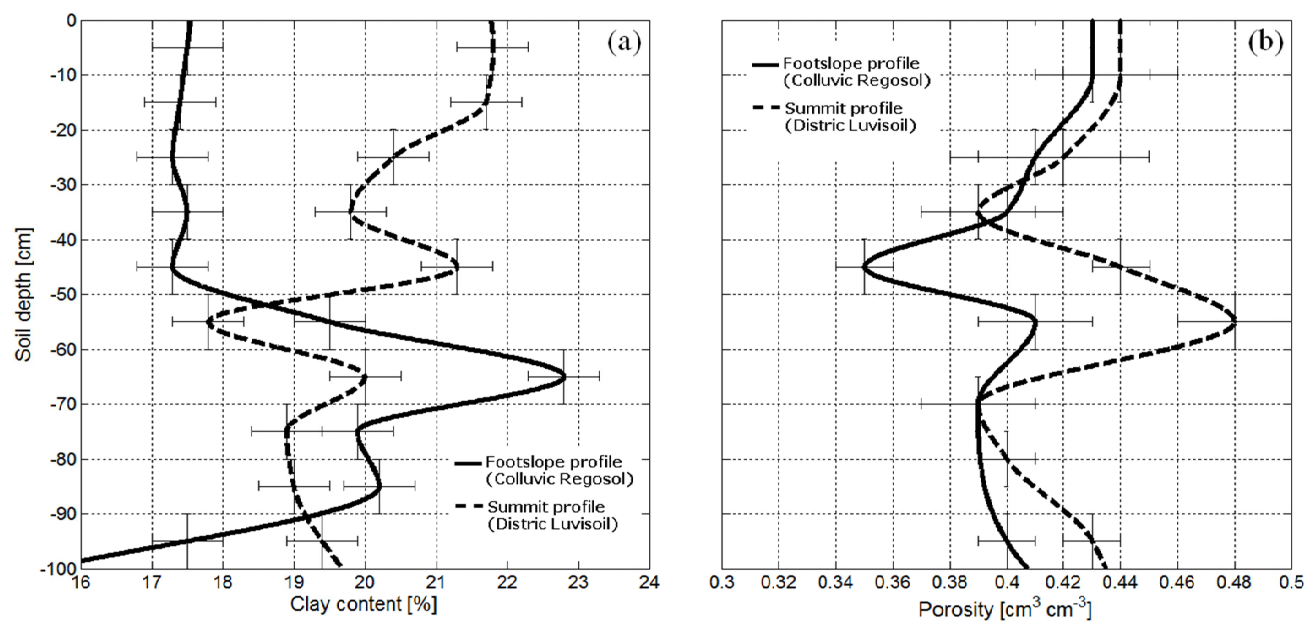


Figure 5.3. Soil physical properties at the footslope (plain line) and at the summit (dashed line) position : (a) Clay content ; (b) Porosity.

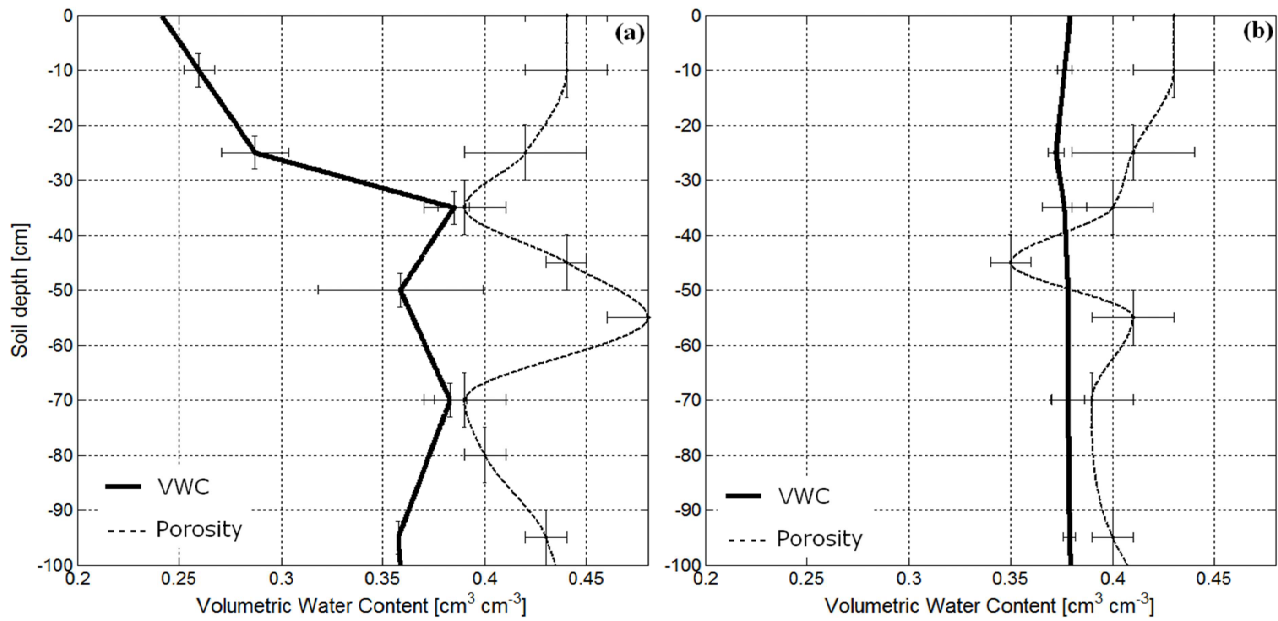


Figure 5.4. Example of soil volumetric water content (VWC) and porosity profiles at DOY 196 in 2013 at the footslope (a) and at the summit position (b). Averaged observations are illustrated by dots. Errorbars give standard deviations on triplicate measurements. Continuous plain lines are linearly interpolated values.

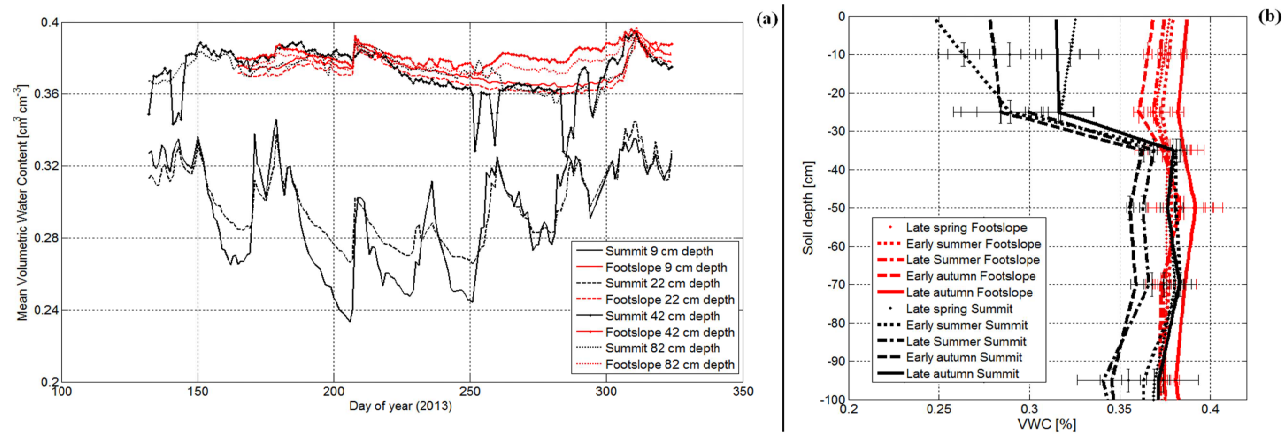


Figure 5.5. Space-time dynamic of soil volumetric water content at the summit (red) and the footslope (black) position in 2013: (a) time series at different depths; (b) Profile at different dates.

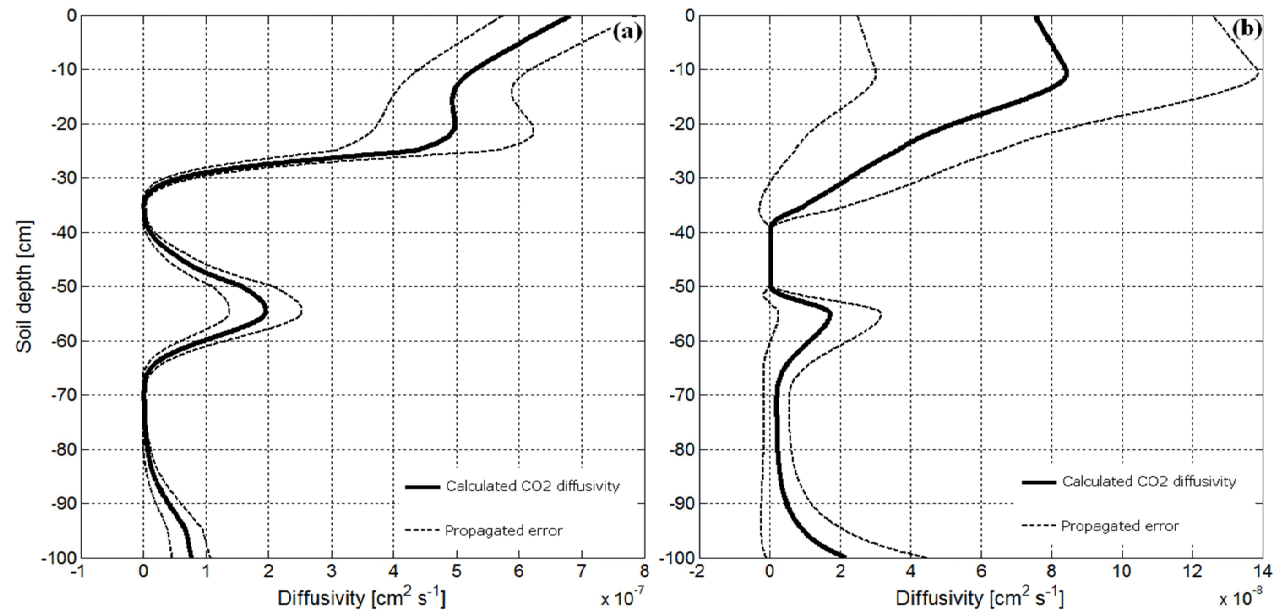


Figure 5.6. Example of calculated soil CO₂ diffusivity profiles at DOY 196 in 2013, at the footslope (a) and at the summit position (b). Dashed lines illustrate the uncertainty range around calculated diffusivity.

5.3.3. Correspondence between directly measured and profile-based surface CO₂ fluxes

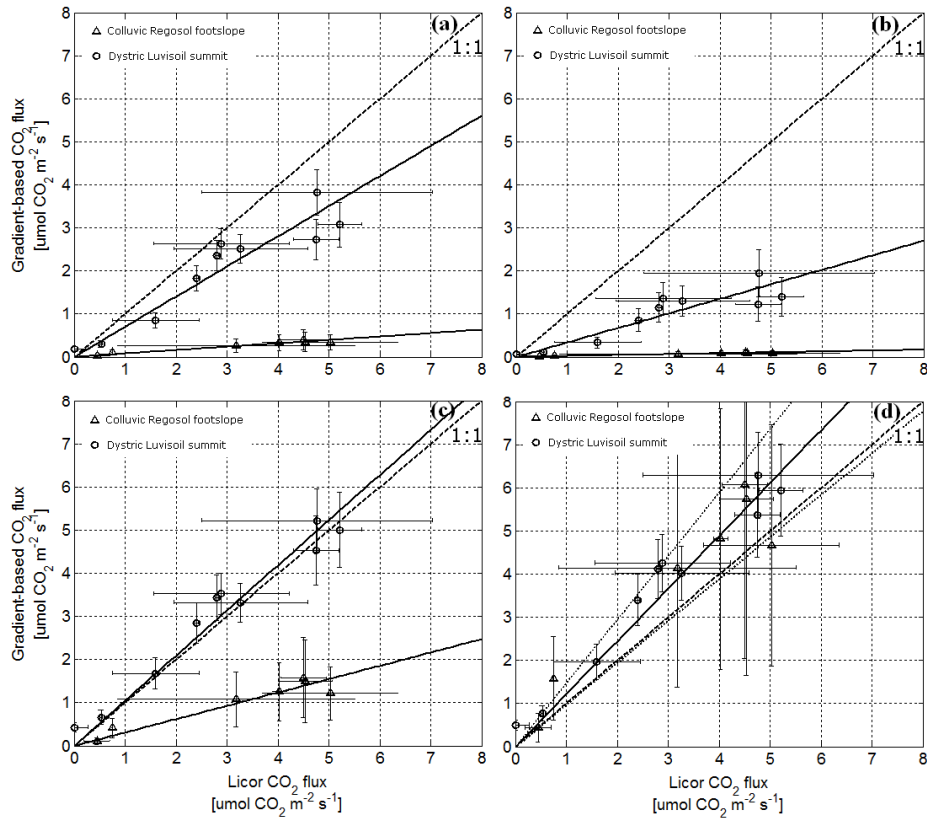


Figure 5.7. Agreement between soil surface CO₂ fluxes directly measured with surface survey chambers (horizontal axes) and calculated according to the gradient-based method (vertical axes), using four different diffusivity models: (a) Millington and Quirk (1961); (b) Moldrup et al (1997); (c) Moldrup et al (1999); (d) Moldrup et al (2000). The plain straight lines are fitted regressions. The dotted straight lines (d) represent a 25% relative error interval around the fitted regression.

Based on Figure 5.7 and Table 5.3, we can see that soil surface CO₂ fluxes directly measured with IRGA chambers and calculated according to the

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gradient-based method are only in good agreement (both good regression coefficient and low over- or under-estimation) if the Moldrup et al. (2000) model is used for the calculation of the soil gas diffusivity. In this specific case, if all data are considered (both summit and footslope soil types), the regression coefficient reaches 92 % (Table 5.3 and Figure 5.7d). The fitted linear regression in Figure 5.7 d shows that gradient-based CO₂ fluxes data are on average overestimated by 22% of the surface measured value ($Y=1.22X$, Table 5.3). Nearly all data are in a variability range of 25% of the relative error around this regression. This means that once corrected for this 22 % overestimation, the gradient-based CO₂ fluxes are at the maximum 1.25 higher or 1.25 lower than the CO₂ fluxes directly measured with surface survey chambers.

When considering all data together (both summit and footslope soil types), we observe that the Millington and Quirk (1961), Moldrup et al (1997) or Moldrup et al (1999) diffusion models results in poor predictions (Table 5.3). If data are considered soil type by soil type (Colluvic Regosol footslope and Dystric Luvisol summit separately), we observe that the regression coefficients all exceed 81%, and this for any diffusion model (Table 5.3). However, when comparing the data by soil type, we observe that the bias is different for the Millington and Quirk (1961), Moldrup et al (1997) and Moldrup et al (1999) diffusion models (Table 5.3). Gradient-based CO₂ fluxes are especially strongly underestimated at the footslope data, as they only correspond to a few percent of the reference IRGA chambers fluxes. Hence, for instance, when using the Moldrup et al (1999) diffusion model, at the summit position, there is nearly no bias ($Y=1.05 X$, Table 5.3), while at the footslope gradient-based CO₂ fluxes are strongly under-estimated ($Y= 0.31 X$, Table 5.3).

The spatial variability coefficient (ratio between standard deviation and mean value) of surface CO₂ fluxes measured with surface survey chambers ranges from 4 to c. 77%, with a median variability coefficient of c. 27%. The variability associated to gradient-based calculated CO₂ fluxes with the Moldrup et al (2000) diffusion model ranges from 15 to 89% of variability coefficient, with a median variability coefficient of c. 23%.

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Table 5.3. Parameters of the regression lines between soil surface CO₂ fluxes directly measured with surface survey chambers (horizontal axes) and calculated according to the gradient-based method (vertical axes), using four different diffusivity models.

	R²	Slope
	[%]	[-]
Millington and Quirk (1961)		
Dystric Luvisoil summit	88	0.70
Colluvic Regosol footslope	93	0.08
All points together	20	0.41
Moldrup et al (1997)		
Dystric Luvisoil summit	81	0.34
Colluvic Regosol footslope	93	0.02
All points together	17	0.19
Moldrup et al (1999)		
Dystric Luvisoil summit	95	1.05
Colluvic Regosol footslope	89	0.31
All points together	36	0.71
Moldrup et al (2000)		
Dystric Luvisoil summit	95	1.25
Colluvic Regosol footslope	89	1.19
All points together	92	1.22

5.4. Discussion

5.4.1. A new analytical function for CO₂ concentration

As shown in Figure 5.2, the selection of the analytical function to interpolate between measured CO₂ concentrations will largely impact the flux calculation both at the surface and at any depths along the soil profiles, as already suggested by Koehler et al. (2010) and Maier and Schack-Kirchner (2014).

Until now, most CO₂ profile studies focused on surface soil layers, with the deepest CO₂ concentration measurements located at 12, 16 and 22 cm (respectively for Pingintha et al., 2010, Tang et al., 2003 and Turcu et al., 2005). Exploring deeper soil layers (i.e. up to 65 cm depth), Gaudinski et al. (2000) demonstrated that the CO₂ concentration profile was better characterized by an exponential model than by a linear one. However, they also suggested that this simple exponential model remained imperfect. Measurements from much deeper layers (i.e. 11 m) illustrated the complexity and the temporal dynamic of CO₂ concentration profiles (e.g. Reardon et al., 1979). Here, we show that a simple decreasing exponential model is not suitable to fit the data when soil layers deeper than c. 42 cm are accounted for, especially at the footslope position (Figure 5.2). Our results show that measurements taken at relatively large depths in the soil profile (i.e. 82 cm) are very informative when estimating the shape of the CO₂ concentration profile (Figure 5.2). The measured CO₂ profile exhibits an inflection point at 40 to 80 cm depth (Table 5.1). This supports the need, highlighted by Maier and Schack-Kirchner (2014), to account for analytical functions which account for this possible curvature change along the concentration profile.

As a novelty, this study suggest that a double sigmoidal equation (Eq. 5.2 and Figure 5.2) better describes the complete soil CO₂ concentration profile (R^2 going from 97 to 100%, Table 5.1) as compared to a simple exponential equation (Davidson et al., 2006; Gaudinski et al., 2000; Maier and Schack-Kirchner, 2014), at least for some typical soils of the European loess belt

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studied here. This observation is suitable all along the year (in 2013) for a wide range of hydrological conditions (Fig 6 and Table 5.1). This mathematical equation simply corresponds to the sum of two sigmoidal curves which differ from each other in both the sharpness of the curve and the departure points on the soil depth (z) axis (Eq. 5.2). The advantage of this fitting analytical function is its capacity to mimic a simple decreasing exponential function in cases where no curvature changes are observed. In this study, the inflection in the CO₂ concentration profile is remarkable at the footslope Colluvic Regosol, while nearly unperceived at the summit Dystric Luvisol (Figure 5.2b and 6b, respectively). Hence, this equation can be suitable for a wide range of soil CO₂ concentration profiles.

On a physical point of view, this double sigmoidal CO₂ profile model (Eq. 5.2 and Figure 5.2) can be justified and linked to other soil attributes: the inflection in the CO₂ concentration profile may correspond to the combined effects of (i) a gas diffusion barrier (Fig. 5.6), associated with high VWC (Figure 5.4) and with locally compacted soil layers (Figure 5.3 and Table 5.2), and (ii) a stimulated CO₂ production in some specific soil layers, also possibly associated with higher or lower VWC (Figure 5.4, Wiaux et al., 2014b).

This gas diffusion barrier would lead to a local accumulation of the CO₂ produced in deeper layers. Such a gas diffusion barrier was previously suggested by Johnson et al. (1994) and more recently highlighted by Koehler et al. (2010). This is also supported by recent studies, showing that soil pore continuity and size are likely to have an increasing role in understanding mechanisms of greenhouse gases production, transport and release (Ball, 2013; Maier et al., 2011).

The stimulated soil respiration in specific soil layers may be related to the presence of an important soil OC stock up to 1 m depth (Wiaux et al., 2014a) providing an important amount of substrate for soil micro-organisms respiration. Therefore, at the footslope position, the concentrations in CO₂ at c.

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42 to 82 cm depth respectively shift from c. 3.0 to 7.9%, while the shift at the summit position is only from c.1.5 to 2.5% between these two soil depths.

5.4.2. Specific measurement ranges to each soil depths

We further show in this study that soil CO₂ concentrations can be very high below the surface horizons of eroded deposits of loamy soils under temperate climate conditions. This relates to availability of large soil OC stocks at these depths (Wiaux et al., 2014a). Depending on the date, CO₂ concentration at 100 cm depth reached c. 1.2 to 3.4 % or c. 4.5 to 8.8 %, respectively for the summit and the footslope positions (CO_{2,∞}, Table 5.1). In contrast, values observed by Davidson et al. (2006) did not exceed 1.2 % at 60 cm depth. This a.o. implies that the measurements of CO₂ concentrations deeper in the soil can encounter technical limitations due to the limited measurement range of currently available probes adapted to in-situ measurements (i.e. GMP343) (Pingintha et al., 2010). Even if technical adaptations are made to increase the measurement range (i.e. GMM222) in in-situ wet conditions, researchers should pay due attention to the selection of the higher measurement limit (e.g. Young et al., 2009).

5.4.3. A unique diffusion model for two contrasted soils

Recent studies (e.g. Ball, 2013; Maier et al., 2011) highlighted the importance of soil structural properties on soil CO₂ diffusion and emissions. Hence, it has also been suggested that the gradient based method largely depends on the selection of the soil gas diffusion coefficient model (Maier and Schack-Kirchner, 2014 ; Pingintha et al., 2010). However, each study applying the gradient-based method uses a different empirical model to calculate the relative gas diffusion coefficient. Maier and Schack-Kirchner (2014) highlighted that no universal best diffusion model exist, but only a specific diffusion model that represents the respective soil. Our results suggest that soil specificity of the diffusion model can be obtained when using a model that integrates the soil specific soil moisture retention characteristic. This latter characteristic can robustly be

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assessed by means of the ϵ_{100} and b parameters, obtained by fitting the Campbell (1974) model of SWR curve to the SWR observations. We strongly recommend using the Moldrup et al. (2000) diffusion model, based on these Campbell (1974) parameters, as this allows to use of the gradient-based method for surface CO₂ fluxes calculation applied to two contrasted soil profiles (both summit Dystric Luvisol and footslope Colluvic Regosol). Hence, this also enables to compare fluxes on different soil types, calculating these fluxes following the same methodology (i.e. same diffusion model) (Figure 5.7 d). Note that our study has specifically focused on typical soils of the European loamy loess belt. However, this diffusion model has also been used successfully in different gradient-based studies, inside (e.g. Goffin et al., 2014) our outside this loess belt (e.g. Davidson et al., 2006).

Comparing four different diffusion models for soil surface CO₂ fluxes calculation (Figure 5.7 and Table 5.3), we show that fluxes directly measured with surface survey chambers and calculated according to the gradient-based method are in good agreement ($R^2=92\%$) for all soil types together only when soil specific diffusion coefficients are used that account for the site-specific physical structure and hydrodynamic properties of the soil pore system. This is quantified by means of 2 soil hydrodynamic parameters that determine the shape of the SWR curve (Moldrup et al., 2000). Hence, the SWR curve is used as a proxy of site-specific soil structural related features.

Note that the Moldrup et al. (1999) model, based on texture characterization, only provides a good quality of prediction when applied to the summit Dystric Luvisol profile (Figure 5.7 d). Our study also supports the choice of the Moldrup et al. (1997) model suggested by Pingintha et al. (2010), but only for the Dystric Luvisol. We demonstrates that this model entails a strong underestimation of gradient-based CO₂ fluxes for other soil types (i.e. Colluvic Regosol, Table 5.3 and Figure 5.7 c). Tang et al. (2003) still obtained better regression coefficients between surface chambers and gradient-based assessments using the Millington and Quirk (1961) model. Based on our results

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(Table 5.3 and Figure 5.7 a), we would not recommend using this model for any soils considered in this study.

Using the Moldrup et al. (2000) diffusion model, the fitted linear regression shows that gradient-based CO₂ fluxes data are in average only overestimated by 22 % of the actual value (Table 5.3). This is lower than the median variability coefficient of c. 27% of spatial variability of surface CO₂ fluxes measured with surface IRGA chambers. This is also lower than the median variability coefficient of c. 23% due to the uncertainty associated to gradient-based calculated CO₂ fluxes. Hence, the gradient-based CO₂ fluxes calculated using the Moldrup et al. (2000) diffusion model can be considered as statistically equivalent to directly measured CO₂ fluxes obtained using the surface survey chambers. However, for better accuracy, data can be adjusted with a correction factor. In our specific study case, calculated gradient-based CO₂ fluxes should be divided by a correction factor of 1.22 to ensure accuracy (consistency with surface chamber flux measurements).

5.5. Conclusions

We suggest a new analytical function, i.e. a double sigmoidal model equation, instead of a simple decreasing exponential, to describe the CO₂ concentration profile in the vertical heterogeneous soils studied here. This indeed provides better fits of the observed CO₂ concentrations, given the curvature change occurring between c. 40 and 80 cm depth. This inflection point in the CO₂ concentration profile was especially marked at the footslope Colluvic Regosol. From a physical point of view, this can be explained by both a gas diffusion barrier (associated with high VWC and locally compacted soil layers) and a stimulated respiration due to higher amount of soil OC at the footslope relative to the summit. This gas diffusion barrier would lead to a local accumulation of the CO₂ produced in deeper layers.

Comparing four different diffusion models for soil surface CO₂ fluxes calculation, we show that fluxes directly measured with surface survey

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chambers and calculated according to the gradient-based method are in good agreement ($R^2=92\%$) for all soil types together only when soil gas diffusion coefficients are used that account for the site-specific physical structure and hydrodynamic properties of the soil pore system. Hence, we recommend using the Moldrup et al. (2000) diffusion model, as it is the only one until now which yields consistent results with surface CO₂ flux measurements at two contrasted soil profiles both typical of loamy soils of the European loess belt (i.e. a footslope Colluvic Regosol and a summit Dystric Luvisol). This allows comparing soil CO₂ fluxes at sites characterized by different soil types using a unique methodology.

Finally this study confirms that the gradient-based method remains subjected to important uncertainties (i.e. the relative error may reach 25%). For controlling this uncertainty, it is of paramount importance to make precise assessments of the soil physical and hydrodynamic properties. In this study, high standard deviations of gradient-based surface CO₂ fluxes were due to the high uncertainties associated with the diffusivity coefficients. This uncertainty was especially high in case of wet conditions in the autumn at the colluvial footslope. For the same reason, replicate measurements of soil CO₂ concentrations are needed.

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6. Quantification of the hillslope scale soil CO₂ fluxes¹

6.1. Introduction

Current large scale estimations of the exchange of C between the soil and the atmosphere are associated with large uncertainties (Houghton et al., 2003, 2007; Peters et al., 2010). Both modelling and experimental approaches have been applied to assess C exchange fluxes at large spatial scales. Yet these approaches are subjected to substantial limitations: (i) the current technical possibilities to measure directly hillslope aggregated CO₂ fluxes are limited (e.g. Baldocchi, 2003), and (ii) the complexity of processes at the scale of a whole catchment is not fully considered in current models of C at the soil-atmosphere interface (Chaopricha and Marín-Spiotta, 2014; Trumbore and Czimczik, 2008).

In-situ measurements of the hillslope aggregated CO₂ fluxes has been largely achieved using the Eddy-Covariance technique (e.g. Goulden et al., 1996; Eugster et al., 2010), but this technique is not appropriate for sloping landscapes, providing an uncertainty on the CO₂ fluxes ranging from 100 to 200 g C m⁻² yr⁻¹ at such non-ideal sites (Baldocchi, 2003). At the local scale, more

¹ Adapted from the following peer-reviewed publication:

Wiaux, F., Van Oost, K., Vanclooster, M., (2014). Quantitative estimation and vertical partitioning of the soil carbon dioxide fluxes at the hillslope scale on a loess soil. **Biogeosciences** Discuss. 11, 13699-13737.

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precise technologies such as survey chambers with infra-red gas analyzers (IRGA) (e.g. Davidson et al., 2002) or such as the non-dispersive infra-red (NDIR) probes (e.g. Young et al., 2009) can be used. However the support scale and spatial resolution of these devices are often too small to make robust large scale assessment of C exchanges across the soil atmosphere interface.

Alternatively, soil modeling of OC dynamics allows assessing the heterotrophic soil respiration (e.g. Herbst et al., 2008). Such models simulations have already been used to calculate the hillslope aggregated CO₂ fluxes (e.g. Dai et al., 2012). However, the predictive capabilities of the models are limited because they do not account for the varying topography and biophysical conditions across the landscape (Dai et al., 2012), and because some key mechanisms controlling the soil CO₂ efflux are not sufficiently implemented in current OC dynamic models: (i) the physical controls on CO₂ fluxes, e.g. gas diffusion barriers along soil profiles, (e.g. Ball, 2013; Maier et al., 2011; Wiaux et al, 2014c – chapter 5 of this thesis); and (ii) the contribution of buried OC at downslope depositional areas to soil C emissions (e.g. Van Oost et al., 2012; Wang et al., 2014; Wiaux et al., 2014a - chapter 3 of this thesis).

While the transfer of soil OC by erosion has been recognized (e.g. Quinton et al., 2010; Stallard, 1998), its impact on both local and global C budgets is poorly understood (Lal 2003), and consequently not implemented in OC dynamics models. Once brought at the bottom of the slope, sediments deposits enriched in soil OC accumulate and are progressively buried deeper and deeper along the soil profiles, forming colluvic soils at the depositional site, with an increasing soil OC stock (Van Oost et al. 2005a, Van Oost et al. 2005b; Van Oost et al., 2012; Wiaux et al., 2014 a - chapter 3 of this thesis). However, a series of complex and interacting processes are acting in these depositional sites, able to decrease as well to enhance mineralization (Lal 2003; Wiaux et al., 2014b - chapter 4 of this thesis). Recent studies (Rumpel and Kögel-Knabner, 2011) highlighted that deep soil OC is highly processed, and showed the need to study more in details the C fluxes coming from deep soil horizons. Recently, through a vertical partitioning of CO₂ fluxes along soil profiles, some authors

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(Takahashi et al., 2004; Davidson et al., 2006; Goffin et al., 2014) showed that the 30 first centimeters of soil significantly contribute to the total surface CO₂ flux. However, to our knowledge, such a vertical partitioning has never been carried out neither in larger scale agro-ecosystems nor in downslope colluvium with buried OC in deep soil layers.

In this study, we aim to quantify the soil-atmosphere C flux at the scale of a hillslope. More specifically, we aim to evaluate two key mechanisms able to improve this estimation of the hillslope aggregated CO₂ fluxes: (i) the persistence of OC in deep colluvium deposits through a vertical partitioning of soil CO₂ fluxes; and (ii) the physical controls on CO₂ fluxes along soil profiles.

6.2. Material and methods

6.2.1. Study site description

The study site and the overall experimental set-up have been described in details in chapter 2. Here, we selected 2 measurement stations along the hillslope: one at the summit and one at the footslope position. The soil properties of these two soil profiles have been characterized in chapters 2, 3 and 6 (Figures 3.3 and 6.3b).

6.2.2. Monitoring of soil CO₂, water and temperature

We measured soil CO₂ concentrations by means of specific designed soil CO₂ probes. The CO₂ sensor in the probe is based on the CARBOCAP® Single-Beam Dual Wavelength non-dispersive infra-red (NDIR) technology (GMM221, Vaisala corp., Vantaa, Finland). Analytical precision is 1.5% of the measurement range added to 2% of the observed value. The sensor was covered with nylon and PTFE (polytetrafluoroethylene) membranes and encapsulated in a tube to avoid soil particles entering the sensor and to limit water infiltration, as illustrated by Figure 5.1 and further detailed by Wiaux et al. (2014c, chapter 5 of this thesis).

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Soil temperature was monitored using a thermistor probe (Therm107, Campbell Scientific Lt., UK). Analytical precision is 0.4°C. Soil volumetric water content (VWC) was monitored using Time Domain Reflectometry (TDR) probes. Topp's equation (Topp et al., 1980) was used to determine VWC, from the apparent dielectric constant measured by TDR probes, as further described in Wiaux et al. (2014c, chapter 5 of this thesis).

Water, temperature and CO₂ concentration profiles measurements were recorded with an automatic data logger (CR1000, Campbell Scientific Lt., UK), connected to a multiplexer (AM16/32, Campbell Scientific, Campbell Scientific Lt., UK).

At each of the 2 slope positions, we measured soil CO₂ concentrations profiles at 4 soil depths with 3 replicates at each depth (Figure 2.8). Vaisala CO₂ probe concentrations ranges were adapted to each soil depth and to each slope position. This allowed to characterize the entire range of values without impacting the quality of observation in terms of precision. At the summit position, measurements ranged between 0-2 % at 12, 25, 45 cm depth and between 0-5 % at 85 cm depth. At the footslope position, measurement ranged between 0-5 % at 12 cm depth, between 0-10 % at 25 and 45 cm depth and between 0-20% at 85 cm depth.

For soil VWC profiles, at each of the 2 slope positions, 18 measurements were collected (6 soil depths, 3 replicates). Sampling depths for VWC were 10, 25, 35, 50, 70 and 95 cm (Figure 2.8). For temperature, 4 soil depths (10, 25, 45, 85 cm) without replicates were measured (Figure 2.8).

To obtain an equilibrated soil environment around the soil concentration probe, we started measurements 1 month after the probes installation. Hourly time-series measurements along soil profiles were performed in 2012 from 12 May to 13 December at the footslope and from the 2nd of June until the 13 December at the summit, and in 2013 from 14 May at the summit and 14 June 2013 at the footslope until 22 November 2013 at the two stations. In 2012,

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some CO₂ measurements were not always possible due to sensors failures and unsuitable measurement range of some sensors.

The measurement plots were covered with a synthetic permeable geotextile during the complete measurement period (Figure 2.8). This avoided vegetation growth and any autotrophic contribution to the soil respiration.

6.2.3. Calculation of the CO₂ fluxes

The procedure for calculating the CO₂ fluxes are explained in details in chapter 5, section 5.2.5. Here, we specifically used the Moldrup et al. (2000) model to calculate soil CO₂ diffusion. This model was shown to provide the most accurate and precise results (Davidson et al., 2006; Goffin et al., 2014; Wiaux et al., 2014c - chapter 5 of this thesis).

6.2.4. Data treatments and adjustments

To optimize the quality of the soil concentration data time-series, observations corresponding to battery voltage lower than 11.5 V were removed. Soil profile CO₂ concentrations measurements were a posteriori corrected for temperature variations using the empirical formulas described by Tang et al. (2003). This allowed removing the impact of temperature on the CO₂ reading of the CO₂ probe, since the CARBOCAP® technology is temperature dependent. Probe specific parameters values for these correction formulas were provided by the probe manufacturer (Vaisala corp., Vantaa, Finland).

Triplicate VWC and CO₂ concentrations data were averaged, providing unique values for each depth, representative of the entire slope position. Soil temperature and VWC profiles were calculated using a linear interpolation between the depth specific values. Surface values were not extrapolated, and were considered as being equal to the closest observations in the profiles. CO₂ concentrations profiles were generated by fitting a decreasing double sigmoidal model to the observations as described in the previous sub-section. The performance of this model (Eq. 2) was evaluated using the regression

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coefficient (R^2). When R^2 values of the fitted CO_2 profiles were lower than a threshold value of 95%, the gradient of CO_2 concentration was considered as unreliable and CO_2 fluxes were not calculated at that time.

We calibrated the diffusion model by adjusting the parameters related to the gas diffusion coefficient (i. e. b and ε_{100}) such that calculated fluxes fit punctual CO_2 fluxes observations. These observations were obtained by means of a portable infra-red gas analyzer with an automated closed dynamic chamber (LI-8100A system, LI-COR, United-States), following Davidson et al. (2002). The sampling design of these surface chamber CO_2 fluxes measurements on the same study site has been described in Wiaux et al. (2014 b, chapter 4 of this thesis). The regression coefficients of the relationship between both measured surface chamber and calculated CO_2 fluxes ensure the consistency (and consequently the precision) of the calculated fluxes (i.e. $R^2=92\%$ both in 2012 and 2013). The slope of the fit (i.e. 1.05 and 1.22, respectively in 2012 and 2013) was used to correct the calculated fluxes and to ensure accuracy, as explained in Wiaux et al. (2014c, chapter 5 of this thesis).

CO_2 fluxes, as assessed by the gradient based method, were calculated on an hourly time-scale, and then integrated on a daily basis. Temperature, VWC, diffusivity and CO_2 concentration values were so averaged on a daily basis.

6.2.5. Vertical partitioning of CO_2 fluxes

The space-continuous CO_2 fluxes profiles obtained using. Eq. 5.2 (chapter 5 of this thesis) were partitioned into 10 slides of 10 centimeters along the soil profile. For each soil slide, we calculated the difference between top and bottom fluxes. This difference was then divided by the total CO_2 flux (e.g. the value at the soil surface). This provides the relative contribution in terms of both CO_2 production and transfer (in %) of each soil slide to the surface CO_2 flux.

In order to allow an easy representation of the temporal dynamic of this vertical partitioning, values were averaged on semi-seasonal time-scale.

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Standard deviation values reflect the variability in time during each semi-season.

6.2.6. Interpolation and aggregation of CO₂ fluxes in time and space

Field measurements were carried out during limited time periods, and hence would not allow assessing the C budget at the whole year scale. In order to obtain continuous time-series covering the entire yearly periods, an OC dynamics model was used as a tool to interpolate and extrapolate measured data of VWC, temperature and CO₂ fluxes for the period of 3 years (2011-2013). Then, we integrated the daily simulated CO₂ fluxes for each of the three studied years. These yearly CO₂ fluxes were averaged over the three studied years and compared between slope positions. The mean yearly CO₂ flux obtained at the summit position was considered to be representative of a non-sloping landscape. To calculate mean yearly CO₂ fluxes representative of a hilly landscape, we calculated a weighted average CO₂ flux of the summit and the footslope, thereby considering the fact that the footslope colluvium represents c. 35% of the surface area of the hillslope.

6.2.6.1. Description of the SoilCO₂-RothC model

The SoilCO₂-RothC model has been described in detail by Herbst et al. (2008). The model combines the coupling of a one-dimensional water, heat and CO₂ flux model (SOILCO₂, Simunek and Suarez, 1993) with a pool concept of carbon turnover (RothC, Coleman and Jenkinson, 1996) for the prediction of soil respiration. The performance of this model was previously evaluated by Herbst et al. (2008) based on a 8 years data set of CO₂ fluxes measurements, and its predictions were judged to be acceptable (with a difference of 0.007 g C m⁻² d⁻¹ between measured and simulated mean daily respiration rates).

This model was run on a daily time step for a period of three years (2011-2013), both for the summit and the footslope positions. Other temporal resolutions (i.e. hourly and weekly time steps) were evaluated but provided poor results.

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The unsaturated soil water flux is described by the Richards equation, and both the soil water capacity and unsaturated hydraulic conductivity function are calculated according to Van Genuchten (1980). Heat transport is implemented according to Simunek and Suarez (1993). Transport of soil CO₂ is simulated considering diffusion and convection in the gas phase, as well as dispersion and convection in the liquid phase. For CO₂ diffusion in the gas phase, we implemented the new Moldrup et al. (2000) model (Eq. 5.4) which was shown to be appropriate for calculating CO₂ fluxes (Davidson et al., 2006; Goffin et al., 2014; Wiaux et al., 2014c - chapter 5 of this thesis).

For the production of CO₂, we only considered two different OC pools on the five ones allowed by the RothC model concept. First, all OC pools in our soils were supposed to participate to C dynamic processes, and hence the inert organic matter (IOM pool) was kept to zero. Then, we assumed the absence of both fresh and resistant plant material (DPM and RPM pools). Hence, the RPM pool was kept to zero, while the DPM pool, characterized by a high decomposition rate constant, was used to represent the labile OC pool (NaOCl-extracted OC, as defined in chapter 3 for the soils studied here). As we did not discriminate here between primary (i.e. vegetal origin) and secondary (i.e. microbial origin) sources of OM, the biomass concentration (BIO pool) was supposed to be included in the labile OC pool, and hence kept to zero. The stable OC pool (NaOCl-resistant OC, as defined in chapter 3 for the soils studied here) was represented in the RothC model by the humus pool (i.e. HUM) which has a low decomposition rate constant. Reduction factors functions are used to simulate the effect of CO₂ concentration, water pressure head, and temperature on the CO₂ production according to the original version of the SOILCO2 model, as described by Simunek and Suarez (1993).

For the boundary conditions for the soil hydrological balance, we used meteorological data, i.e. precipitation and evapo-transpiration at the top of the soil profiles, and a free drainage concept at the bottom of the soil profiles. Precipitations were directly measured in a meteorological station close to our study site (c. 2 km). At the summit, we considered a run-off production once

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input water flux exceeds the infiltration capacity, while at the footslope we specified that water can accumulate at the soil surface. Daily evapotranspiration was calculated according to the Penmann-Monteith equation, based on measured meteorological data. The boundary conditions of soil heat flow were defined using directly measured soil temperature both at the top and at the bottom of the soil profile.

6.2.6.2. Model parameterization and calibration

In this study, 5 soil depth increments were considered for the two studied soil profiles, i.e. 0-18 cm, 19-30 cm, 31-45 cm, 46-70 cm, and 71-100 cm depth. These increments were chosen to consider the depths where measurements probes were installed and the soil structural properties (Wiaux et al., 2014a - chapter 3 of this thesis). The soil hydrodynamic parameters of the van Genuchten – Mualem function (Mualem, 1976; van Genuchten, 1980), as well as parameters related to the gas diffusion coefficients (i.e. b and ε_{100}) are specified for each soil material. The initial concentration of the labile and stable OC pools were specified for each soil material, as presented in Wiaux et al. (2014a, chapter 3 of this thesis). However, these concentrations of OC were aggregated based on the individual soil samples according to this specific depth increments splitting. These OC and soil physical input values were considered as being the same for each profile node of the soil material for which a value was provided.

For identifying the value of input parameters, we calibrated the model using the global inversion model PEST (e.g. Gallagher and Doherty, 2007). We used measured soil VWC, temperature and CO₂ concentration measurements, as well as calculated CO₂ fluxes within the profile to invert the model.

We carried out a simple sensitive analysis of the SOILCO2-RothC model to identify key parameters. Among the more sensitive parameters, which could significantly impact the outputs of the model, we firstly inverted the 9 soil Mualem - van Genuchten parameters, related to VWC, both at the summit and at the footslope. In a second step, we kept them fixed and inverted parameters

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related to soil CO₂ fluxes, both at the summit and the footslope: (i) the 5 initial concentrations of the labile OC pool, (ii) the decomposition rate of the labile OC pool, (iii) the activation energy reflecting temperature sensitivity, as well as (iv) the HB1 coefficient (i.e. the value of the pressure head at which CO₂ production by soil micro-organisms is at the optimal level). Initial concentrations of the labile OC pool were inverted inside a realistic range of values (i.e. average $\pm$ 3 times the standard deviation) as compared to the previous measurements done by Wiaux et al. (2014 a, chapter 3 of this thesis). Initial values and inversion range of activation energy were based on Q₁₀ values identified for each slope position by Wiaux et al. (2014 b, chapter 4 of this thesis), using the relationship between activation energy and Q₁₀ (Craine and Gelderman, 2011; Kätterer et al., 1998). At the footslope, we additionally inverted the 5 ε_{100} parameters related to the gas diffusion.

6.3. Results

6.3.1. Spatio-temporal analysis of measured soil variables

Figure 6.1 shows the spatio-temporal variation of soil temperature, moisture and gas diffusion, and Figures 6.2 and 6.3 shows the spatio-temporal variation of CO₂ concentrations and fluxes. All these values correspond to in-situ measurements during period of c. 6 months in 2013. Similar measurements have been carried out in 2012 and display similar spatio-temporal trends (data not shown).

The soil temperature (Figure 6.1) does not significantly differ between the summit and the footslope, except during July (day of year 180 to 220) where temperatures are c. 2 to 3 degrees higher at the summit while they follow exactly the same temporal dynamic. The surface mean daily temperatures vary all along the soil profiles from 4°C to 28°C at the summit, and from 4°C to 26°C at the footslope (for the period of measurements).

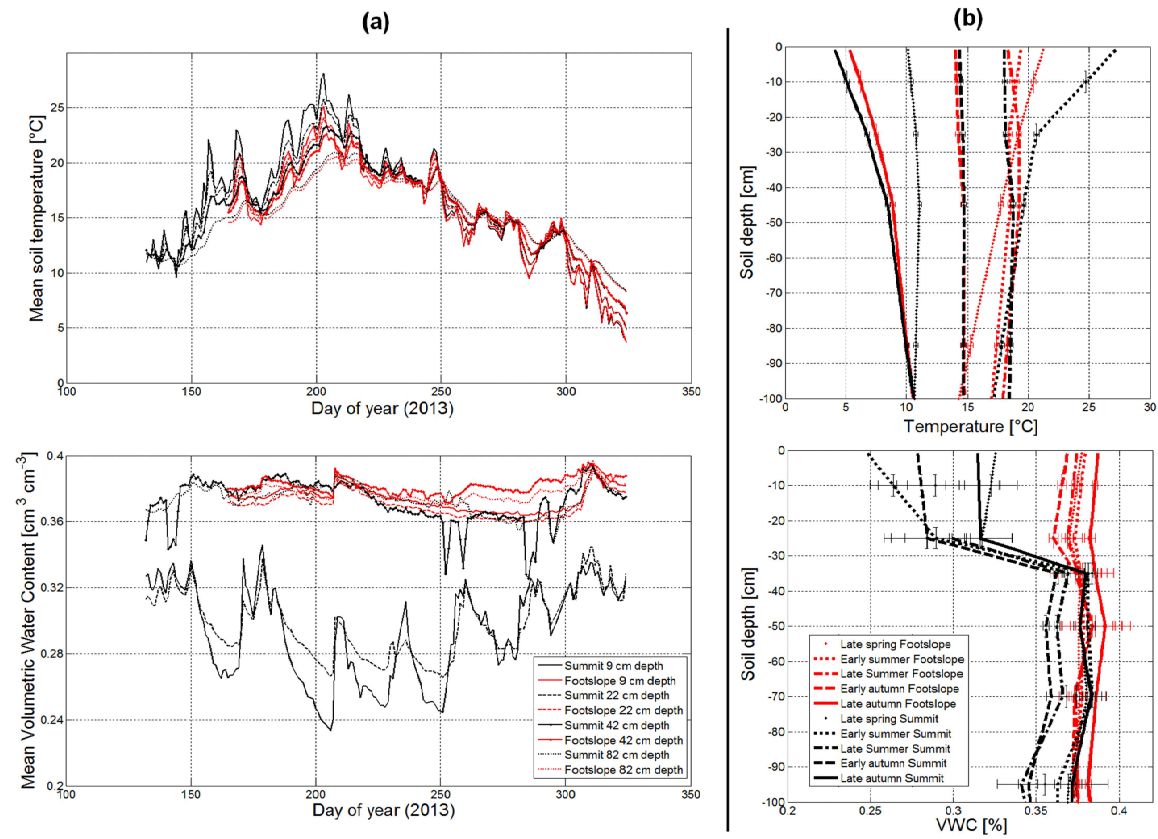


Figure 6.1. Space-time dynamic of soil temperature and moisture at the summit (red) and the footslope (black) position in 2013: (a) time series at different depths; (b) Profile at different dates.

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The space-time dynamics of soil volumetric water content (VWC, Figure 6.1) differ completely between the summit and the footslope. At the footslope, soil VWC values remained inside a narrow interval (36 to 39%) all along the soil profile during the considered period. At the summit, soil VWC varies from 23 to 34% in the plow layer (0-30cm depth) and then increases by an absolute value of 15 to 5% (respectively) in the rest of the soil profile. The soil at the summit position is the wettest during the early spring and the late autumn and driest in the summer. At the footslope soil VWC reaches the saturation level in the early summer after an important rainfall event and then slowly decreases until the early autumn and reaches saturation again in the late autumn. Similarly, in the summer, the soil gas diffusivity (Figure 6.3) reaches its maximum value at the summit while it reaches its lowest value at the footslope. Soil gas diffusivity is c. 10 times lower at the footslope relative to the summit.

Soil CO₂ concentrations (Figure 6.3) are c. 3 times lower at the summit relative to the footslope. Along soil profiles, soil CO₂ concentrations increases with depth, following a double exponential trend as described in Wiaux et al. (2014c, chapter 5 of this thesis). This second exponential curve begins at c. 50 depth, and is especially pronounced at the footslope, reflecting a shift of c. 4% CO₂ between 44 and 100 cm depth. The time course of soil CO₂ concentrations at both the summit and the footslope increases from spring to late summer and then decreases to reach its lowest value in the late autumn.

The CO₂ fluxes (Figure 6.2) were calculated based on both CO₂ concentrations and diffusivity following the method described in Wiaux et al. (2014c, chapter 5 of this thesis). These calculated CO₂ fluxes vary in the same range of values when comparing the footslope and the summit. However, the peaks do not occur at the same period from a slope position to another, with maximum CO₂ fluxes being emitted respectively during summer and autumn for the summit and the footslope. In addition, the duration of these maximum peaks differ between the summit and the footslope. Along the soil profiles, CO₂ fluxes decrease with depth and reach null values at c. 30 cm depth at the summit and at c. 15 cm depth at the footslope.

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The distribution of the soil CO₂ fluxes in the profile is illustrated in Figure 6.4. At the footslope, c. 90 to c. 95 % of the surface CO₂ fluxes is generated in the 10 first centimeters of the soil profile. The soil layer between 10 and 20 cm contribute for only 5 to 10 % depending of the period, and the deeper layers do not significantly contribute to the surface fluxes. At the summit, the relative contribution of the different soil layers is more dynamic in time, with a contribution of the 10 first centimeters of the soil profile ranging from c. 80 % at the late spring, decreasing to c. 60 % in the early summer, and reaching c. 40 % from late summer to the late autumn. At the summit, the 30 first centimeters of the soil profile significantly contribute to surface fluxes. This contribution decreases with depth in the late spring and the early summer, but is homogeneously distributed with depth for the rest of the time. At the summit, soil layers deeper than 30 cm depth sometimes contribute for up to 20% of the total flux, especially in the autumn. Between 40 to 50 cm depth, and 80 to 90 cm depth, some negative contribution (i.e. CO₂ uptake) up to -20% is also observed.

6.3.2. Modeling of surface CO₂ fluxes

Results of the daily aggregated simulation with the SoilCO₂-RothC model are summarized in Table 6.1 and Figure 6.5. The simulated soil temperatures and VWC represent adequately the observations (Table 6.1). The simulated CO₂ fluxes fit well the CO₂ fluxes in 2013, both for the summit and the footslope. This fit is less good at the footslope ($R^2=42\%$, Table 6.1) but it remains acceptable given the quite local shift between observations and model simulations (Figure 6.5). This shift (model underestimation) may be explained by the contribution of soil alkalinity to soil CO₂ fluxes during specific dry events in summer (e.g. Laponis et al., 2008; Wiaux et al., 2014d – chapter 5 of this thesis). Punctual surface CO₂ fluxes measurements (Licor chamber system) extended to daily values corroborate the goodness of fit (GOF) of the simulations in 2012 (Table 6.1 and Figures 6.2 and 6.4).

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Simulated surface CO₂ fluxes (Figure 6.5) remains more or less in the same range of values (from 0 to 6 g C m⁻² day⁻¹ in 2011 and 2013, and up to 8 g C m⁻² day⁻¹ in 2012). However, the temporal dynamic differs between slope positions and between years of simulation, with a clear alternation of peaks of year 2011 and 2013. At the summit, CO₂ fluxes increases from the winter to reach their maximum during the summer and then decreases again (Figure 6.5), similarly to the temporal dynamic of soil temperature (see Figure 6.1 as an exemple). At the footslope, the lowest CO₂ fluxes occur in the middle of the summer of each year, while a very high CO₂ fluxes can be observed from the late summer until the early autumn in 2011 and 2013 as well as in spring of year 2011 (Figure 6.5).

The time integrated CO₂ fluxes are presented in Table 6.2. For the considered a simulation period of 3 years, the footslope emits c. 1.5 more CO₂-C than the summit ($p < 0.01$), which represents an additional flux of $287 \pm 106 \text{ g CO}_2\text{-C m}^{-2} \text{ year}^{-1}$. The uncertainty on model simulations (given by ME values in Table 6.2) remains lower than the difference between slope positions for each year (Table 6.2). Once integrated at the hillslope scale, this means that such a loamy hillslope emit c. 1.2 times more CO₂-C relative to a flat landscape ($p < 0.1$).

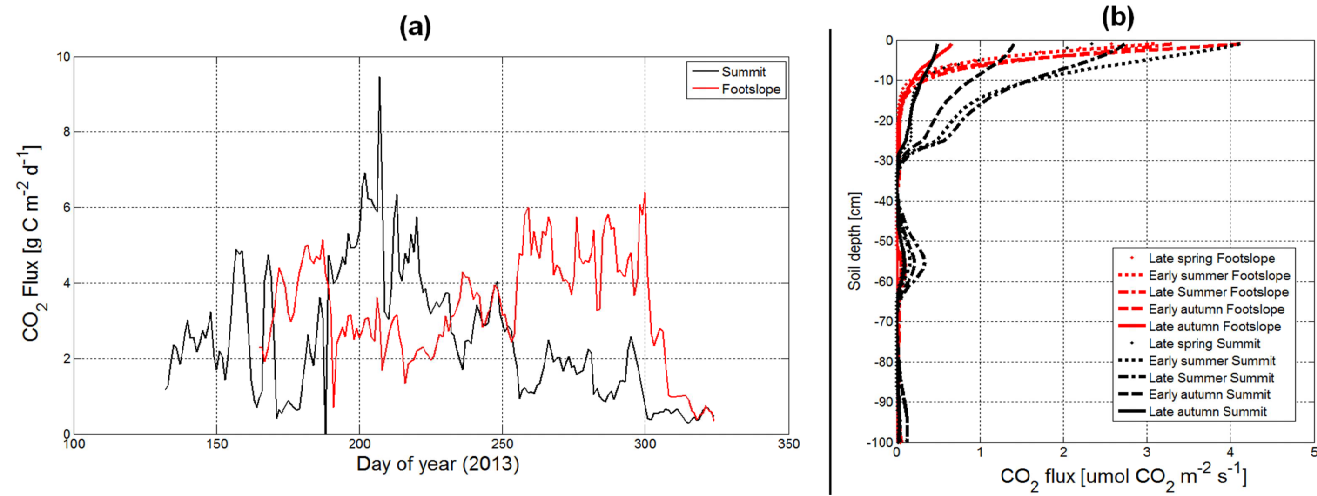


Figure 6.2. Space-time dynamic of soil CO₂ fluxes at the summit (red) and the footslope (black) position in 2013: (a) time series at different depths; (b) Profile at different dates.

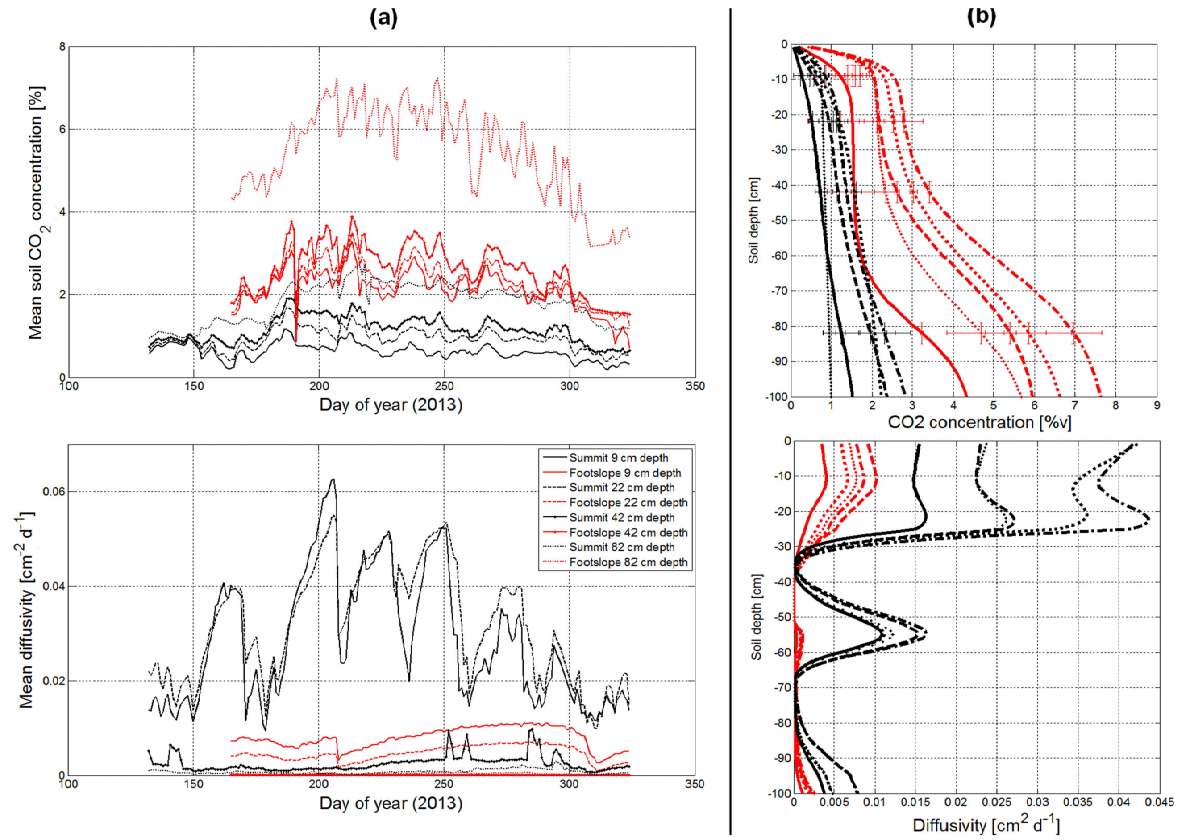


Figure 6.3. Space-time dynamic of soil CO_2 diffusivity and concentrations at the summit (red) and the footslope (black) position in 2013: (a) time series at different depths; (b) Profile at different dates.

Summit
(a)

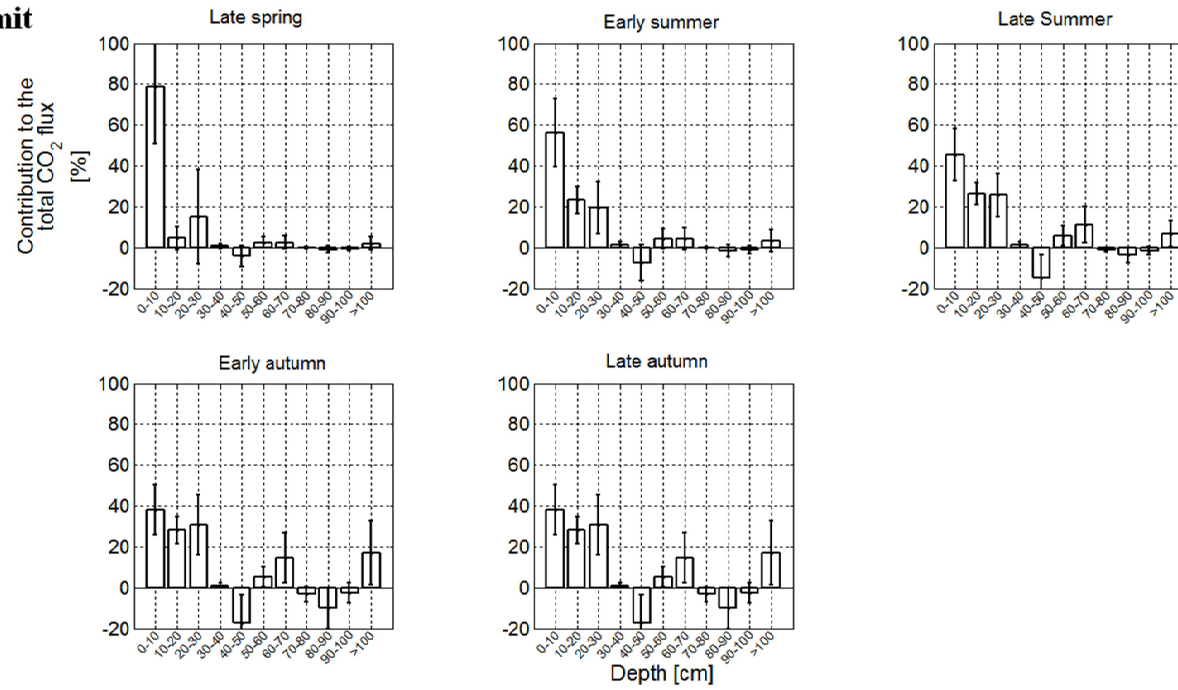


Figure 6.4. (a) Depth distribution of the relative contribution to soil surface CO₂ fluxes in year 2013 averaged by semi-seasons (error bars represent the standard deviation of the time aggregation for each soil layer) at the summit position.

Footslope (b)

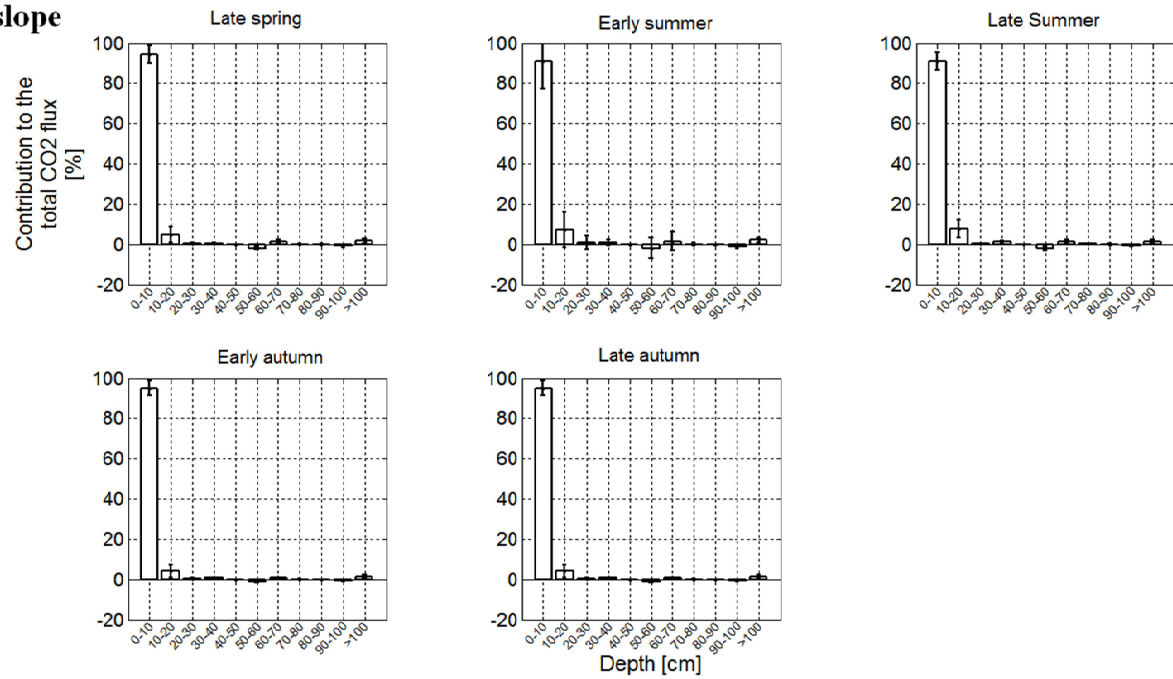


Figure 6.4. (b) Depth distribution of the relative contribution to soil surface CO₂ fluxes in year 2013 averaged by semi-seasons (error bars represent the standard deviation of the time aggregation for each soil layer) at the footslope position.

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Table 6.1. Regression coefficient (R^2 , [%]) between observations and simulations.

VWC [†]		Temperature [†]		CO ₂ flux [‡]	
2012	2013	2012	2013	2012	2013
Summit					
64	73	100	100	63	64
Footslope					
82	89	99	100	61	42

[†] For VWC and temperature, the R^2 value is given as an indication representative of the 10 cm depth soil layer (but similar values are encountered all along the soil profile).

[‡] For CO₂ fluxes, the observations compared to model simulations are punctual surface measurements with the Licor chamber system in 2011 (n=8 days) and 2012 (n=15 days), while it is continuous daily time-series of gradient-based fluxes in 2013 (n= 129 days at the summit, and n=137 days at the footslope). Data are not shown for 2011 (too low number of observations for CO₂ fluxes, no observation for the other variables).

Table 6.2. Yearly simulated CO₂ flux [g C m⁻² year⁻¹] at different slope positions.

	Summit	Footslope	Diff.	Hillslope
2011 (± ME)	545 (- 22)	944 (+26)	399 (+ 4)	685
2012 (± ME)	654 (+ 136)	842 (+63)	188 (- 73)	719
2013 (± ME)	553 (+ 47)	826 (+ 138)	274 (+ 91)	647
Average ± SD	583 ± 61 a***	870 ± 64 b***	287 ± 106	684 ± 36c*

Diff. is the difference between the footslope and the summit yearly CO₂ flux.

ME is the model error (sum of the difference between observations and simulations for each day of the year). A positive value means that model underestimates the flux, and inversely.

SD is standard deviation.

Mean values with different letters are significantly different from each other (Student test, *:0.05<p<0.1; **:p<0.05; ***:p<0.01).

To calculate mean yearly CO₂ fluxes representative of a hilly landscape (hillslope), we achieved a weighted sum of the summit and the footslope fluxes, according to the fact that the footslope colluvium covers c. 35% of the surface of the hillslope.

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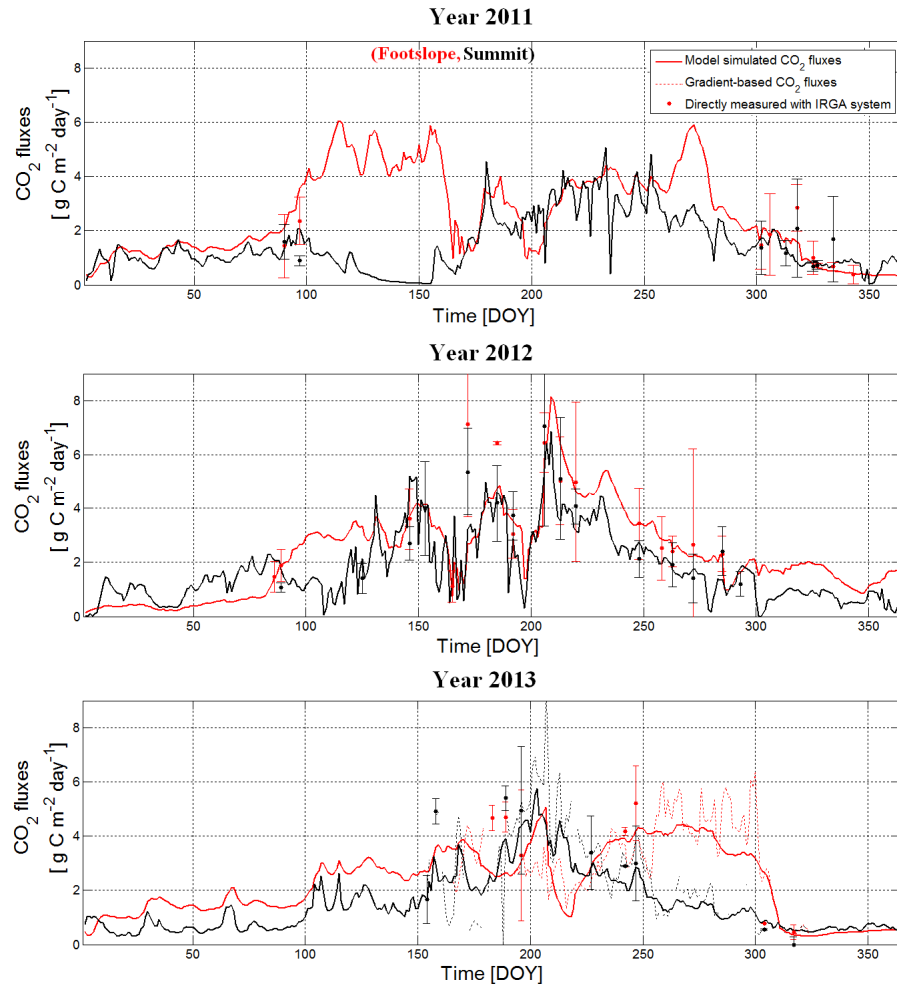


Figure 6.5. CO₂ fluxes from 2011 to 2013 at two slope positions (footslope in red, summit in black): (i) simulation based on the SOILCO2-RothC model (plain lines), (ii) calculated fluxes with the gradient-based method (dashed lines), and (iii) spatial average of in situ measured fluxes with the IRGA Licor chamber (points with errorbars).

6.4. Discussion

6.4.1. Soil physical control on CO₂ emissions

The difference of the temporal dynamic of surface soil CO₂ fluxes between footslope and summit positions, as illustrated in Figure 6.2, indicates that the limiting factors on flux emissions are not the same all along the hillslope. At the summit, on one hand, the dynamic of surface soil CO₂ fluxes clearly follows the temperature variations (Figure 6.1, maximum during the summer). At the footslope, on the other hand, the surface soil CO₂ fluxes (Figure 6.2) are small when the soil is close to water saturation. This is related to the fact that a high water filled pore space disables the transfer of biotic CO₂ along the soil profile (Figure 1). The surface soil CO₂ flux dramatically increases when the gas diffusivity exceeds a threshold value of c. 0.1 cm² d⁻¹ (i.e. from day 255 to 305 of year 2013, Figures 6.2 and 6.3).

In the period preceding this important CO₂ emission, the soil CO₂ cannot move along the soil profile and accumulates within soil pores. This may result in both a CO₂ concentration increase and the dissolution of CO₂ and soil carbonates in the soil solution as DIC. A CO₂ concentration increase was observed both in the early and the late summer, especially below c. 50 cm depth (Figure 6.1). This phenomenon is particularly evident below the compacted soil layer between c. 40 cm and c. 50 cm depth. This is consistent with the porosity profile described by Wiaux et al. (2014c, chapter 5 of this thesis) and illustrated in Figure 6.3b. This also corroborates the results of Wiaux et al. (2014c, chapter 5 of this thesis), suggesting that in downslope Colluvic Regosols, gas diffusion barriers (explained by a compacted soil layers) strongly impact the CO₂ concentration profile, and hence the temporal dynamic of resulting CO₂ flux at the soil surface. This supports recent studies (e.g. Ball, 2013) that showed that soil pore continuity and size are key to understand the mechanisms regulating the soil gases emissions.

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As a consequence, the significantly higher CO₂ concentration at the footslope relative to the summit, especially in deep soil layers, is not explained by the large amount of soil labile OC along the footslope soil profile (Wiaux et al., 2014 a,b – chapters 3 and 4 of this thesis) but is more likely the result of the accumulation along time (during too low diffusivity periods). Maier et al. (2011) showed that the CO₂ efflux can deviate from the instantaneous soil respiration due to CO₂ storage into soil pore spaces. Hence, soil physical variables are dominating the control of surface CO₂ fluxes at the footslope. This supports the conceptual improvement of the SOILCO₂-RothC model realized in this study, and the use of soil specific hydrodynamic parameters to characterize the gas diffusion (Moldrup et al., 2000).

Due to the interactions between variables and the complexity of the above-described system, simple correlation analyses will often not provide satisfactory results when studying soil respiration (Maier et al., 2011; Wiaux et al., 2014 b - chapter 4 of this thesis), especially across sloping landscapes. This highlights the importance to use process-based C dynamic models considering both production and transfer terms (i.e. SoilCO₂-RothC) when studying the soil CO₂ efflux.

In summary, we highlight that the mechanisms which govern soil surface CO₂ emissions vary throughout the landscape. On a well-drained soil at the summit, observed soil CO₂ emissions are directly related to the CO₂ production through the phenomenon of soil micro-organisms respiration. However, on a wet footslope, observed temporal dynamic of soil CO₂ emissions much more reflects the physical transfer mechanisms: long periods of CO₂ production and accumulation alternate with periods of important release at the soil surface.

6.4.2. Soil organic carbon storage in downslope deposits

Soil respiration rate can be interpreted as an indicator of soil OC persistence (e.g. Gregorich et al., 1994). However, a further analysis of what occurs along the soil profile is needed to thoroughly answer the question of the persistence

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of OC. At the footslope, the vertical partitioning of the soil CO₂ fluxes, as illustrated in Figure 7, shows that c. 90 to c. 95 % of the surface CO₂ fluxes originates from the 10 first centimeters of the soil profile. Given the important amount of OC until up to 100 cm depth in our study site (Figure 3.3, Wiaux et al., 2014 a - chapter 3 of this thesis), this observation is not in agreement with the study of Goffin et al. (2014), who suggest that the relative contribution of the soil layers to the surface CO₂ fluxes is related to OC distribution along the soil profile. This higher contribution of the upper soil layers seems to be neither related to higher temperatures values (Figure 6.1), contrary to what was suggested by Takahashi et al. (2004). According to the CO₂ concentration and diffusivity profiles (Figure 6.3), the relative contribution of the soil layers to the surface CO₂ fluxes is more likely governed by soil physical controls (Ball 2013) rather than by biological production depending on thermal energy and OC substrate. Here, soil gas diffusivity strongly decreases from 10 to 40 cm depth (where diffusivity is null) at the two slope positions, and the profile of CO₂ concentration displays no gradient between 10 and 40 cm depth specifically at the footslope (Figure 6.3).

Here, we show that despite the low contribution of soil layers deeper than 10 cm depth (Figure 6.4), the top soil layer (0-10 cm) generates CO₂ fluxes which exceed those observed at the summit position (Table 6.2), due to the major contribution (c. 90%) of the surfacing soil OC to the total CO₂ fluxes at the footslope position (Figure 6.4). This can be explained by environmental conditions specific to this 0-10 cm layer playing in favor of both microbial respiration and gas diffusion. Indeed, close to the soil surface, both diffusion barriers and limitation of the access to the oxygen disappear. Hence, the only residual impact of soil VWC on soil respiration is its positive effect due to the increased access of soil micro-organisms to their OC substrate, and to the enhancement of their metabolic activities by water (Akinremi et al., 1999; Castellano et al., 2011; Herbst et al., 2008; Howard and Howard, 1993; Šimůnek and Suarez, 1993). The combination of this high amount and high quality of soil OC (Figure 3.3, as described by Wiaux et al., 2014a - chapter 3 of this thesis)

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with this net positive effect of soil VWC results in a strong increase of microbial respiration rates.

Our results suggest that buried soil OC in colluvial deposits is stored for a long time below 10 cm depth, which corroborates the assumption of a long-term stabilization of deeply buried OC in downslope colluviums suggested in the literature (Doetterl et al., 2012; Berhe et al., 2008, 2012a). Hence, despite that deep soil OC (e.g. in colluvial deposits) has been shown to be highly processed (Rumpel and Kögel-Knabner, 2011), our results suggest that this OC turnover occurs in a closed soil sub-system that is potentially disconnected from the atmospheric C pool. This explains why the total and labile soil OC pools remain important and homogeneously distributed along the soil profile at the footslope, while it exponentially decreases with depth at the summit (Figure 3.3, as described by Wiaux et al., 2014a - chapter 3 of this thesis).

Some studies suggest that net C sequestration occurs at the depositional sites (e.g. Smith et al. 2005), while others negate the apparent C sink caused by soil OC burial at depositional sites (e.g. Yoo et al. 2005). Here, our results reconcile two seemingly contradictory assertions: (i) buried soil OC at a footslope is efficiently stored in the subsoil and submitted to a long-term stabilization (Doetterl et al., 2012; Berhe et al., 2008, 2012a), and (ii) the footslope profile emits more CO₂ than the summit (Reicosky et al., 2005; Webster et al., 2008b; Wiaux et al., 2014b - chapter 4 of this thesis).

6.4.3. Quantification of soil-atmosphere CO₂ fluxes at the hillslope scale

Despite the fact that peaks of CO₂ fluxes are the highest at the summit position, cumulative CO₂ fluxes are the highest at the footslope position from year 2011 to 2013 (Figure 6.5). As a consequence, the total annual flux averaged along 3 years of simulation is c. 1.5 times higher ($p < 0.01$) at the footslope relative to the summit (Table 6.2). These observations are consistent with the results of Webster et al. (2008a; 2008b) in forest fields, who observed 1.6 higher median

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respiration fluxes at footslope and toeslope positions compared to the crest and convex shoulder positions. These observations are also in agreement with the recent findings Wiaux et al. (2014 b - chapter 4 of this thesis) based on punctual surface Licor chamber measurements on the same site, showing that mean respiration fluxes (standardized at 15°C) were c. 1.3 times higher at the footslope and 1.5 times higher at the toeslope ($p \leq 0.05$) relative to the summit position. The reason of this trend is that factors that control soil OC respiration are heterogeneously distributed across sloping landscapes (Reicosky et al., 2005; Webster et al., 2008b; Martin and Bolstad, 2009; Wiaux et al., 2014 b - chapter 4 of this thesis).

Our estimations of annual CO₂ fluxes may be associated with large uncertainties due to error propagation on measured variables. Despite the modest performance of the SoilCO₂-RothC model in reproducing the CO₂ fluxes observation (R^2 ranging between 42 and 64%, Table 6.1), the model uncertainties (given by ME values, Table 6.2) are lower than the difference of annual CO₂ fluxes between slope positions (Table 6.2). In addition, this model error (sum of the difference between observations and simulations for each day of the year) observed in this study (from 4 to 91 g CO₂-C m⁻² yr⁻¹, Table 6.2) are lower than the uncertainty on the CO₂ fluxes directly measured at the catchment scale using the Eddy-covariance technique (from 100 to 200 g CO₂-C m⁻² yr⁻¹ at non-ideal sites like sloping plots, Baldocchi, 2003). Hence, this supports the validity of the quantitative comparison of CO₂ fluxes between slope positions carried out in this study.

Focusing on CO₂ fluxes aggregated at the scale of the entire hillslope, such a loamy hillslope emits 683 ± 36 g CO₂-C m⁻² year⁻¹ while a flat landscape would only emits 583 ± 61 g CO₂-C m⁻² year⁻¹ (Table 6.2). Hence, for our study site, accounting only for soil C dynamics representative of flat landscapes would under-estimate annual soil-atmosphere CO₂ exchanges by c. 20 %. This supports similar conclusions drawn under a forest eco-system by Webster et al. (2008 a), who highlighted a risk of under- or over-estimation of soil respiration at large scale reaching up to 30% when topography is not accounted

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for. Our results provide a thorough quantification and a better understanding of the soil-atmosphere C exchanges specific to an agro-ecosystem on the loess belt in Belgium, which may be of high importance to adopt strategies to mitigate climate change.

The CO₂ emissions reported in literature studies as soil heterotrophic respiration (Table 6.3) are ranging from c. 170 to c. 456 g CO₂-C m⁻² year⁻¹ in similar conditions (i.e. temperate loamy croplands), from c. 140 to c. 144 g CO₂-C m⁻² year⁻¹ in forests ecosystems, and reach c. 1811 g CO₂-C m⁻² year⁻¹ in temperate grasslands on organic soils. However, most of these studies were carried out on flat landscapes. To our knowledge, no equivalent quantification of the hillslope aggregated CO₂ fluxes already exists for agro-ecosystems. The values of CO₂ emissions presented in this study are in the same order of magnitude but are slightly higher than literature studies on flat croplands (Boeckx et al., 2011; Kutsch et al., 2010; Paustian et al., 1990). This may be explained by the hilly relief of this study site and the lateral transfer of soil particles enriching the downslope area in soil OC (Wiaux et al., 2014a – chapter 3 of this thesis), inducing higher respiration rate relative to a flat uneroded position (Wiaux et al., 2014b – chapter 4 of this thesis).

The higher heterotrophic respiration at our study site compared to other temperate loamy croplands (Table 6.3) could also be explained by some experimental biases: (i) a priming effect due to the land-use change (soil kept bare and undisturbed during 3 years); (ii) any heading due to the dark geotextile installed at the surface of the measurements stations; and (iii) the modest model performances in terms of predictivity (Table 6.1). Hence, the absolute estimation of the hillslope aggregated CO₂ fluxes in this study should be interpreted carefully, and the focus should be on the relative difference between emissions from flat and sloping landscapes (i.e. 20%, Table 6.2).

Quantification of hillslope CO₂ fluxes

Table 6.3. Comparison of yearly soil heterotrophic and total respiration flux [g C m⁻² year⁻¹] in agro and other ecosystems.

Heterotrophic resp.	TER	Landscape relief	Soil type and agri. practice	Measurement technique	Sources (calculated from)
Temperate cropland					
583 ± 61 †	NI	Flat	Luvisoil	Model simulation	This study
683 ± 36 †	NI	Hillslope	Pedological gradient		
456 ‡	585 ± 60	Flat	Luvisoil	Close chamber	(Boeckx et al., 2011)
394 ‡	505 ± 30				
374 ‡	480 ± 20				
170 ‡	230				
250 ‡	350	Flat	Mollic Gleysol (loam)	Close chamber	(Paustian et al., 1990)
290 ‡	400				
302 ‡	1006 ± 222				
309 ‡	1029	Flat	Luvisoil	Eddy covariance	(Kutsch et al., 2010)
Tropical and mountain forests					
140 ‡	180	Hillslope	Pedological gradient	Gradient-based	(Webster et al., 2008a)
144 ‡	480	Hillslope	Loam	Model simulation	(Dai et al., 2012)
Temperate grassland					
1811 ‡	2322	Flat	Organic soil	Close chamber	(Renou-Wilson et al., 2014)
983 ‡	1260				
1354 ‡	1736				

TER = Total ecosystem respiration (heterotrophic and aboveground and belowground autotrophic respiration);

† Direct measurements of soil heterotrophic respiration (bare soil)

‡ Calculated from measurements of soil heterotrophic and belowground autotrophic (roots) respiration AR_b (considering AR_b/TER = c. 22% according to Suleau et al., 2011);

‡ Calculated from measurements of soil heterotrophic and aboveground and belowground autotrophic respiration AR (considering AR/TER = c. 70% according to Suleau et al., 2011).

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In order to understand the impact of these findings in terms of C balance, it is important to compare these heterotrophic respiration fluxes to other soil C inputs and outputs (see chapter 8 – Figure 8.2). Among other things, soil heterotrophic respiration fluxes discussed here only constitute c. 30% of the total ecosystem respiration, also composed of aboveground and belowground autotrophic respiration fluxes (Suleau et al., 2011; Table 6.3) which were not considered here. However, this exceeds the scope of this study and should be explored at the scale of hillslopes in future researches.

Notwithstanding these elements, our results support that, when modeling soil C dynamics and when quantifying soil-atmosphere CO₂ exchanges, this is of paramount importance to consider slopes and elevation effects rather than a flat landscape, and to account for dynamic processes (e.g. lateral transfer of soil OC and heterogeneous distribution of soil VWC) occurring along hillslopes.

6.5. Conclusion

At the summit position of the hillslope, the time course of surface soil CO₂ fluxes clearly follows the time course of temperature (Figure 3, maximum during the summer). At this position of the hillslope, observed soil CO₂ emissions are directly related to the CO₂ production through soil micro-organisms respiration. At the footslope, high water filled pore space disables the transfer of biotic CO₂ along the soil profile, and the surface soil CO₂ flux substantially increases when the gas diffusivity exceeds a given threshold value. Hence, on a wet footslope, the time course of observed soil CO₂ emissions is more determined by the physical transfer mechanisms: long periods of accumulation alternate with periods of important surface release. Considering these elements, the entire hillslope emits c. 20 % more g CO₂-C m⁻² year⁻¹ compared to a similar flat plot. This results support the need to consider slopes when modeling soil-atmosphere C exchanges.

At the footslope, the vertical partitioning of the soil CO₂ fluxes shows that c. 90 to c. 95 % of the surface CO₂ fluxes originates from the 10 first centimeters of

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the soil profile. However, the total annual flux averaged along 3 years of simulation show that the top soil layer (0-10 cm) of the footslope generates CO₂ fluxes which exceed those observed at the summit position. Hence, our results reconcile two seemingly contradictory hypotheses, i.e. (i) these support that soil OC at such a footslope is stored along the main part of the soil profile and submitted to a long-term stabilization, and (ii) at the same time these support that the footslope profile emits more CO₂ than the summit.

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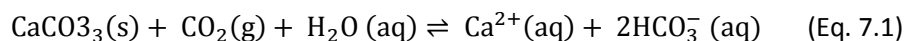
7. Carbonates-related CO₂ fluxes

7.1. Introduction

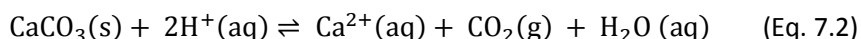
Traditionally, the soil CO₂ flux is assumed to be largely controlled by the biotic process of microbial oxidation of soil organic matter (e.g., Davidson et al., 1998; Lal and Bruce, 1999; Perrin et al., 2004; Wiaux et al., 2014b). However, it has been shown that CO₂ efflux from soils can deviate from the instantaneous soil respiration due to series of abiotic mechanisms (i.e. not related to soil micro-organisms respiration, Maier et al., 2011), acting separately or in combination (e.g. Ball, 2013; Hammerlynck et al., 2014; Risk et al., 2013; Serrano-Ortiz et al., 2010; Takle et al., 2004). Among these, the contribution of soil alkalinity and soil carbonates is not fully understood and need further investigation (e.g. Bertrand et al., 2007; Serrano-Ortiz et al., 2010). Indeed, despite thermodynamic and kinetic processes controlling soil CO₂ fluxes related to soil alkalinity are well established (e.g. Plummer et al., 1979), it remains challenging both to quantify their contribution to total soil CO₂ fluxes, and to understand under which pedo-climatic context it may occur as these fluxes strongly depends on dynamic environmental factors.

Soil alkalinity can be defined as the sum of all species of dissolved inorganic carbon (DIC), including H₂CO₃, HCO₃⁻ and CO₃²⁻. For pH higher than 6.3, a net gaseous abiotic CO₂ emission occurs when soil carbonates precipitate (e.g. Plummer et al., 1979), while CO₂ is consumed during carbonate dissolution, as illustrated by Equation 7.1:

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In acidic conditions (pH<5), CO₂ emission can also be associated with carbonate dissolution (Plummer et al., 1979), as illustrated in Equation 7.2. This is for instance the case when a soil amended with dolomite-lime is acidified (e.g. Hamilton et al., 2007).



Soil carbonates dissolution (Equation 7.1), leading to a net gaseous CO₂ consumption by soils, is associated to an increase of the alkalinity of the soil solution as DIC (e.g. Lapenis et al., 2008; Serrano-Ortiz et al., 2010). While in-situ isotopic analyses have never been conducted to clearly demonstrate it, some observations of net CO₂ uptake by soils support the assumption of the occurrence of this phenomenon in natural ecosystem. This phenomenon likely occurs when leaching water (acting as a reactant in Equation 7.1) dissolves soil carbonates, consumes atmospheric CO₂, and transports DIC downward the soil profile. This can occur either in polar climatic areas (Ball et al., 2009; Parsons et al., 2004; Shanhun et al., 2012, 2013), or in the wet period of cold dry climates (Lapenis et al., 2008), or even during night-time under hot dry climates (Serrano-Ortiz et al., 2010; Xie et al., 2009). At the opposite, many studies conducted either on desert and (semi)-arid ecosystems in hot dry climates (e.g. Dever et al., 1987; Emmerich, 2003; Kowalski et al., 2008; Serrano-Ortiz et al., 2010), or during the hot summer period of cold dry climates (Lapenis et al., 2008) reported some abnormally high fluxes of CO₂ release from soils. These observations have been used to support the occurrence of abiotic CO₂ emissions related to the soil alkalinity (Equations 7.1 and 7.2).

While there is no scientific reason to exclude the occurrence of abiotic CO₂ fluxes related to soil alkalinity and carbonates in temperate and continental climates, these geochemical processes have never been studied and quantified in-situ under these climates. In our study, we aim to document in-situ observations under temperature climate suggesting the significant contribution of soil alkalinity and carbonates to CO₂ fluxes.

7.2. Methodology

We carried out a study in the Belgian loam belt on a sloping cropland under temperate climate (50.6669°N, 4.6331° W). The carbonated loess soil has been weathered, leading to a complete removal of soil carbonates at the summit of the slope (the carbonated C horizon appears at c. 165 cm depth), and a residual concentration of 0.1% and 0.4% at the surface (0-30cm), respectively of the convex slope and the backslope. Both organic and inorganic C stock in each soil layer and each slope positions have been described by Wiaux et al. (2014a).

The surface CO₂ fluxes (corresponding to mixed biotic and abiotic sources) were quantified in-situ with a portable infra-red gas analyzer, with an automated closed dynamic chamber (LI-8100A system, LI-COR, United-States). The autotrophic contribution to respiration is considered as insignificant as the soil was kept bare during the complete measurement period. Measurements were carried out between spring 2011 and winter 2012, with a weekly measurement frequency. At each slope position, 12 measurements were achieved, spread on an area of c. 15 m². In order to calculate average CO₂ fluxes values for each slope position, a Generalized Least Square (GLS) regression model was applied in R-2.14.0 for Windows (R Development Core Team, 2007), considering the spatial correlation between replicates, as further detailed by Wiaux et al. (2014b). CO₂ fluxes data have been standardized at a reference temperature according to a Q₁₀ exponential model (Wiaux et al., 2004b). For our study, we selected a restricted dataset corresponding to the optimal moisture condition (20-30% VWC, i.e. n=56 measurement days) and to the dry conditions (< 20% VWC, i.e. n=5 measurement days) (Wiaux et al., 2014b).

In addition, we simulated the biotic CO₂ fluxes in years 2012 and 2013 by means of the SOILCO₂-RothC model (Herbst et al., 2008), using time-series of gradient-based surface CO₂ fluxes (chapter 5 and 6 of this thesis) to calibrate it, and in-situ measurements of soil OC pools, VWC and temperature as model inputs.

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Note that the measurement period of the surface CO₂ fluxes data standardized for temperature and analyzed in them (between spring 2011 and winter 2012) is different than the period of model simulations (years 2012 and 2013). Unfortunately, model simulation in 2011 are associated with too important uncertainties due to the low number of measurement to calibrate the model, and cannot therefore not be used in them self to demonstrate any effect of carbonates in CO₂ fluxes.

7.3. Results and discussion

Observed CO₂ fluxes normalized at reference temperature of 15°C (Table 7.1) are 47 to 58% higher under very dry conditions (i.e. <20%VWC) than under optimal moisture conditions, while we would expect the inverse tendency as the highest respiration fluxes should occur under 25 to 27 % volumetric water content (Perrin et al., 2004; Bauer et al., 2012, Wiaux et al., 2014b). Indeed, dry conditions limit the activity of soil micro-organisms (e.g. Herbst et al. 2008; Wiaux et al., 2014b) as (i) soil water content increases the access of soil micro-organisms to their OC substrate, and (ii) soil micro-organisms need water for their own metabolic activities.

The simulated respiration rates using the SOILCO2-RothC model (summit position in 2012 and 2013) only explain 61% (R^2 coefficient) of the total variability of observed surface CO₂ fluxes (Figure 7.1). More precisely, at the beginning of the summer season (day of year 170), the average value of surface CO₂ fluxes exceed the simulate respiration rates at three different dates by a factor of c. 2.

Our results (Table 7.1 and Figure 7.1) suggest that CO₂ fluxes observation cannot always be explained by biological processes only, and highlight that sometimes, under specific environmental conditions, at least c.50% of the observed CO₂ flux does not come from soil respiration (biotic origin) but are more likely due to carbonates precipitation (abiotic origin).

Carbonates-related CO₂ fluxes

Table 7.1. Comparison of directly measured soil surface CO₂ fluxes (standardized at a reference temperature of 15°C) under dry (<20%VWC) and optimal moisture (20% < VWC <30%) conditions, averaged in space and time along years 2011 and 2012.

Measurement station	Spatio-temporal averages of surface CO ₂ fluxes [$\mu\text{mol m}^2 \text{s}^{-1}$]				Abiotic part of flux (b-a)/b [%]
	Optimal moisture conditions (a)	Drought conditions (b)	CO ₂ fluxes difference: (b)-(a)	Difference significance	
Summit	1.42 ± 0.19	3.38 ± 0.49	1.96	P<0.001	> 58
Convex shoulder	1.97 ± 0.26	3.74 ± 0.50	1.71	P<0.05	> 47
Backslope	2.60 ± 0.34	1.97 ± 0.70	-0.63	Not sign.	/

Other abiotic CO₂ sources than soil alkalinity are not likely here. Recently, Serrano-Ortiz et al. (2010) suggested that high abiotic CO₂ emissions under hot and dry climates would be explained by alternating wet and dry periods at a daily time-scale (due to diurnal high evapotranspiration phases), inducing subsurface CO₂ storage during the night and subsequent degassing during the day. This is not likely to occur under temperate climates where temperature range is not broad enough and evapotranspiration rates remains low relative to hot and dry climates (Williams et al., 2012). In addition, measurements presented in Table 7.1 were taken in the middle of a dry period, were no gas diffusion barriers would have induce preliminary CO₂ storage into soil pores (e.g. Ball, 2013). For similar reasons, pressure pumping (Takle et al., 2004) and diurnal fluctuations in temperature causing expansion and contraction of soil atmosphere (Hammerlynck et al., 2014) are neither realistic. In addition, our experimental setup (i.e. a LI-COR dynamic chamber with a special vent designed to eliminate the Venturi effect that appears under windy conditions) ensures that no wind ventilation effect can occur, as suggested by Risk et al. (2013).

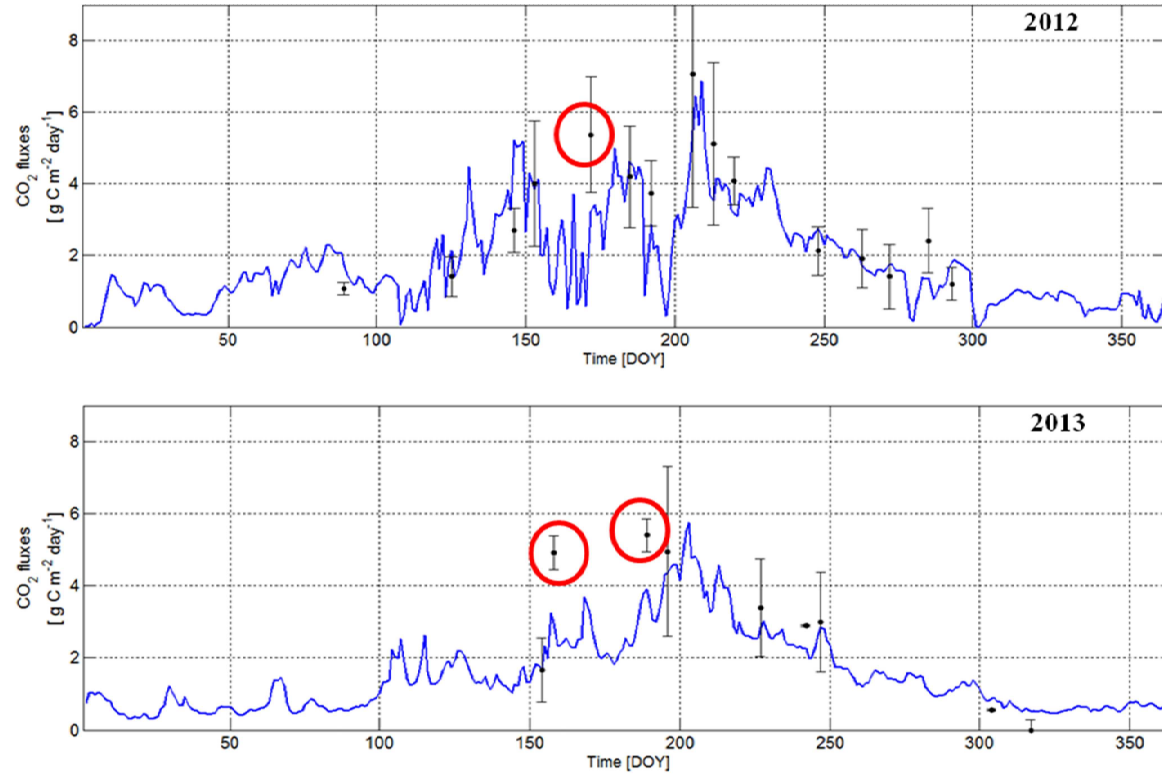


Figure 7.1 Surfaces CO₂ fluxes in 2012 (top) and 2013 (bottom) at the summit: (i) the blue line represents the simulated respiration based on the SOILCO2-RothC model; (ii) blacks points with errorbars are in-situ measured CO₂ fluxes with a dynamic chamber (not standardized for temperature); (iii) the red circle points out the measured CO₂ fluxes which do not match with the model simulation of soil respiration.

Carbonates-related CO₂ fluxes

According to Eq. 7.1 and to similar studies under other pedo-climatic contexts (i.e. steppe in cold and arid climate, desert in hot and arid climates, and polar climates) the precipitation of pedogenic carbonates and the associated abiotic CO₂ emissions observed here may be explained by the combined effects of different environmental factors: (i) a temperature increase which entails a decrease of the CO₂ solubility in water (i.e., degassing, according to the Henry's law) (Ball et al., 2009; Laponis et al., 2008; Serrano-Ortiz et al., 2010), (ii) the increased evapotranspiration stimulating the upward capillarity movement and the associated advection of both DIC and Ca ions which concentrate in the upper soil layers, pushing the equilibrium of Equation 1 to the left (Laponis et al., 2008).

Our observations corroborate the recent findings of Buysse et al. (2012). Based on laboratory incubation experiments of limed loess soil, these authors suggest that the contribution of soil alkalinity to CO₂ can sometimes range from 20 to 100% under temperate climate at some specific time-dependent environmental conditions. The alternating abiotic CO₂ emission and uptake due to soil carbonates dissolution and precipitation (respectively), combined with the heterotrophic respiration (both processes being controlled by temperature variations) would explain the hysteresis effect sometimes observed in the exponential relationship between temperature and soil CO₂ emissions (Buysse et al., 2012).

As calcite of loess soils (widespread under temperate climatic areas, e.g. Rommens et al., 2005) is c.10⁸ times more soluble (Appelo and Postma, 1994) than dolomite of calcareous soils (often found in desertic ecosystems under hot dry climates, e.g. Emmerich et al., 2003), the highest amount of carbonates do not show the highest contribution of alkalinity to the CO₂ flux, and inversely (Bertrand et al., 2007). Hence, the low content in soil carbonates observed here is not a reason to exclude the fact that they may cause significant CO₂ emissions. Even at the summit where no soil carbonates are observed at the surface, DIC and Ca ions may originate from the bottom of the profile (c. 165 cm depth) where dissolution of the carbonated loess occurs.

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Recrystallized pedogenic carbonates stones (e.g. Gocke et al., 2010) were found locally along the soil profiles (Figure 7.2). These carbonates stones were only observed in the carbonated C horizons (below 150 cm and 100cm depth and at the soil surface, respectively at the summit, at the shoulder and at the backslope positions). This is an additional piece of evidence that geochemical processes involving soil alkalinity and soil carbonates occur under temperate climate, and potentially play a role in abiotic CO₂ emissions.



Figure 7.2. Recrystallized pedogenic carbonates stones found locally at different depths along the soil profiles (unit of the measuring-tape in centimeters).

7.4. Concluding remarks

Our results suggest the occasional occurrence of abiotic CO₂ fluxes due to soil alkalinity under temperate climatic conditions, potentially contributing for up to c. 50% of the total flux under some specific time-dependent environmental conditions. This highlights the importance to further study the processes controlling the contribution of soil alkalinity and carbonates to CO₂ fluxes, especially under temperate and continental climates. Under these temperate or continental climatic contexts, other hypotheses about the explanation of abiotic CO₂ fluxes must also be explored, including pressure pumping (Takle et al., 2004), diurnal fluctuations in temperature causing expansion and contraction of soil atmosphere (Hammerlynck et al., 2014), and the role of evapotranspiration and soil physical controls (Maier et al., 2011; Serrano-Ortiz et al., 2010).

The geochemical processes described here may significantly impact the global C cycle. While seasonal cycles of carbonates precipitation and dissolution are likely to compensate each other in the yearly C budget (e.g. Liu, 2011), some authors suggest that yearly CO₂ consumption can exceed CO₂ release (Wohlfahrt et al., 2008), because of DIC exportation from the soil system to the rivers (Raymond and Cole, 2003), or because IC is isolated in deeper soil layers as newly recrystallized carbonates (Gocke et al., 2010). The magnitude of this specific alkaline abiotic CO₂ flux is poorly studied and quantified, and therefore need further investigation to better model the global C budget.

Future researches should focus on the quantification of this abiotic CO₂ fluxes related to soil carbonates and soil alkalinity. Stable isotopic C signatures ($\delta^{13}\text{C}$) have been widely used to discriminate between the origin (inorganic or organic) of CO₂ fluxes in laboratory experiments (e.g. Bertrand et al., 2007). However, the isotopic calculation methods should be adapted to account for a conceptually layered soil. The soil concentration and isotopic signature of CO₂ sampled at a given depth are, in general, the result of the production of CO₂ at this given depth and the vertical diffusion through soil pores of soil CO₂

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produced deeper in the soil profile. In addition, the results provided by stable isotopic techniques is sometimes based on weak theoretical assumptions, a.o. considering that isotopic signature of IC both in the liquid and the solid phases are equal, and that no isotopic C fractionation occurs between the source substrate and the product of chemical reactions. Many challenges have therefore to be taken up and the technologies related to stable isotopes have to be developed in the field of in-situ quantification and discrimination between biotic and abiotic CO₂ fluxes sources.

8. Summary and conclusion

8.1. Main research findings

Note that the experiments and conclusions presented in this thesis are specific to a unique study site described in details in chapter 2. While this is a methodological and statistical limitation to directly extent our conclusions to larger scales, this was a judicious choice which could not be circumvented to explore into details the mechanistic processes acting on soil OC persistence. Despite this scale limitation, we argue that the processes observed here occur along most of sloping croplands under temperate climatic conditions on the western part of the European Loess belt given the: (i) similar temperature ranges and averages, (ii) similar meteorological conditions leading to high moisture level at downslope positions; and (iii) the similar pedological gradients and geomorphological contexts, as illustrated in other studies (e.g. Brahy et al., 2005; Doetterl et al., 2013; Reyniers et al., 2006).

Through the different experiments achieved during this thesis, we highlighted that the mechanisms governing soil OC persistence and soil-atmosphere CO₂ emissions vary throughout the landscape, and we demonstrated the impact of these relief-dependent controls on the C cycle. More precisely, we obtained five main research findings that are summarized below.

Chapter 8

First, erosion-induced downslope buried OC stock has been stabilized until now, mainly due to local wetter hydrological conditions.

The hillslope was exposed to intensive soil erosion, leading to a transfer of soil material to the footslope (i.e. cumulative soil truncation of c. 2 m at the backslope position and c. 1.3 m at the convex shoulder position). Deposition of the eroded material resulted in the formation of a colluvial soil at the footslope position, significantly enriched in soil OC. The footslope has a significantly higher (c. 2.5 times, $p < 0.01$) stock of total OC ($9.0 \pm 1.0 \text{ kg OC m}^{-2}$) when compared to the other slope positions (chapter 3).

The soil OC concentration remains important and homogeneously distributed along the soil profile at the footslope, while it exponentially decreases with depth at the summit (chapter 3). We found that c. 90 to c. 95 % of the surface CO_2 fluxes at the footslope originates from the 10 first centimeters of the soil profile (chapter 7). These results support the notion that buried soil OC in footslopes is efficiently stabilized, at least under the conditions encountered in our study site (chapter 7).

Due to the lack of oxygen for the microbial community as a result of water filling soil pores, this long-term stabilization of the soil OC stock can be explained by the negative effect of soil moisture on soil respiration under wet conditions (i.e. above 25% VWC) (chapter 4). This inhibition of OC decomposition does not occur in the surface layer (0-10 cm) where soil micro-organisms have easy access to oxygen, despite the higher VWC values (chapter 7). Hence, OC persistence is not only related to its chemical composition or associations, but is controlled by the specific environmental conditions, i.e. soil moisture conditions (chapter 4).

Summary and conclusion

Second, soil OC stocks in downslope positions are not stabilized due to their intrinsic bio-chemical properties, but instead, by the local environmental conditions. As a result, this store may be quickly released as CO₂ to the atmosphere if protecting environmental conditions change in the future due to disturbances related to changes in climate and/or land management.

We showed a strong spatial differentiation of the labile OC pool (i.e. the OC not resistant to NaOCl) along the hillslope with a significant enrichment at the depositional site (labile OC stock of 5.8 ± 0.2 kg OC m⁻²). The labile OC pool contributed for $64 \pm 5\%$ to the total OC at the footslope, against $49 \pm 6\%$ for the summit (chapter 3). This is due to both the low amount of reactive mineral phases that could link with OC to stabilize it, and the saturation effect of these reactive minerals in soils due to the important quantities of OC (chapter 3). Hence, a large part of this depositional OC stock has a high potential for mineralization given both its higher quantity and quality (chapter 3).

In addition, in chapter 4, we highlighted that the large stock of OC stored in colluvial soils has a higher temperature sensitivity ($Q_{10}=3.72\pm0.17$) than in non-depositional slope positions ($Q_{10}=1.77\pm0.18$ to 2.59 ± 0.13). We indeed pointed out an exponential increase of temperature sensitivity with increasing soil VWC, explaining the higher Q_{10} values in wet depositional areas (chapter 4).

Given all these elements, we conclude that the OC stored in colluvial soils is particularly vulnerable to OC mineralization under drier and/or warmer conditions or in situation where the buried sediment is resurfaced (e.g. by increased erosion). When considering the large amount of OC that has been buried globally as a result of agricultural erosion during the last decades (e.g. Van Oost et al., 2005a), the long-term stability of this pool under future land use and/or climate disturbance is an area of concern.

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Third, high water filled pore space values at the footslope create diffusion barriers which disables the transfer of biotic CO₂ along the soil profile, explaining why the time course of the CO₂ efflux is not directly linked to the time course of the soil respiration.

The space-time dynamics of soil VWC (chapters 4 and 7) differ completely between the summit and the footslope, with higher values and narrower ranges of VWC at the footslope (e.g. in the 0-30cm layer, 36 to 39% at the footslope vs. 23% to 34% at the summit). As a result, soil gas diffusivity (chapter 7) is c. 10 times lower at the footslope than at the summit. Hence, on a well-drained soil at the summit of a hillslope, the observed time course of soil CO₂ emissions is directly related to the CO₂ production through the soil micro-organisms respiration. In contrast, on a wet footslope, the soil C efflux is much more determined by the physical transfer mechanisms, inducing long periods of CO₂ accumulation alternating with important release at the soil surface.

This physical control may explain why the impact of water content on soil respiration appears as negative under wet conditions (i.e. >25% VWC), despite VWC has a positive impact on soil respiration under dryer conditions where soil gas diffusivity is allowed (chapter 4).

Hence, the calculation method of soil gas diffusivity is of paramount importance. The Moldrup et al. (2000) diffusion model is based on site specific hydrodynamic parameters. Relative to three other well-known diffusion models, this model provided the best agreement ($R^2=92\%$) between CO₂ fluxes directly measured with surface survey chambers and CO₂ fluxes calculated according to the gradient-based method (chapter 6). The SOILCO2RothC model was conceptually improved relative to its current version, by implementing this way to calculate the diffusion coefficient (chapter 7).

Summary and conclusion

Fourth, the CO₂ efflux is affected by the soil alkalinity and pedogenic carbonates precipitation, especially in summer dry periods. Further studies are needed to explore this area of concern.

As reviewed in chapter 5, the abiotic CO₂ emissions were already observed in a wide range of other climatic areas and explained by the increased evapotranspiration stimulating the upward capillarity movement and the associated advection of both DIC and calcium ions which concentrate in the upper soil layers, pushing the equilibrium in favor of carbonates precipitation and associated CO₂ emissions. Inversely, during winter or spring wet periods, leaching water dissolves soil carbonates and consumes atmospheric CO₂.

The abnormally high CO₂ fluxes occurring under dry conditions (chapter 4) may be explained by this alkalinity-related CO₂ fluxes (chapter 5). The differences (especially marked during the summer) between observed and modeled CO₂ fluxes (chapter 7) may also be explained by a significant contribution of these geochemical processes in the total CO₂ emissions (chapter 5).

Fifth, current rates of heterotrophic respiration are c. 30% to c. 50% higher at the bottom of the slope than at the top, demonstrating the need to consider landscape effects when modeling and quantifying soil OC dynamics.

The heterogeneous spatial distribution of environmental controls on soil CO₂ fluxes along the hillslope (chapters 2 - 3 - 4 - 7), explain the c. 30% to c. 50% higher respiration rates observed at the footslope (chapters 4 and 7). Indeed, the large stock of labile OC found at the bottom of the slope results in enhanced soil respiration, while this effect is substantially suppressed by the wetter soil conditions at the same slope position (chapter 4). Despite the low contribution of soil layers deeper than 10 cm depth due to this suppressing water effect, the top soil layer (0-10 cm) generates CO₂ fluxes which exceed those observed at the summit position (chapter 7). At the footslope position, the major contribution (c. 90% to 95 %) of the total CO₂ fluxes comes from the surfacing soil OC (chapter 7).

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When modeling soil C dynamics and when quantifying soil-atmosphere CO₂ exchanges, these results support the need to consider slopes and elevation effects, and to account for dynamic processes (e.g. lateral transfer of soil OC and heterogeneous distribution of soil VWC) occurring along hillslopes. For our study site, accounting only for soil C dynamics representative of flat landscapes would under-estimate annual soil-atmosphere CO₂ exchanges by c. 20 %.

8.2. Overall conclusion

Our research findings support that considering soils as mobile systems (Quinton et al, 2010) is of paramount importance to establish the C budget of the soil-atmosphere system.

The impact of processes that occur at the landscape scale (i.e. vertical and lateral redistribution of sediment, associated C, water and energy) on soil carbon turnover is quite complex to establish, as it requires a deep understanding of series of mechanistic and spatio-temporal dynamic processes occurring across the landscape. These were studied as detailed as possible in this thesis, leading to the following overall conclusion.

In a first instance, depositional areas, and to a larger extent entire hillslopes, have to be considered as erosion-induced C sinks, as deeply-buried OC can be stored during very long time-scales in these downslope colluviums, acting as geomorphological pumps of CO₂ (Stallard et al., 1998). At least under the conditions encountered in our study site, we showed that buried soil OC at the footslope is efficiently stabilized: the soil OC concentration remains important and homogeneously distributed along the soil profile and that c. 90 to c. 95 % of the surface CO₂ fluxes at the footslope originates from the 10 first centimeters of the soil profile. However, the physical accumulation and burial in itself is not sufficient to ensure the long-term stabilization of OC. Indeed, the OC persistence results from combined effects of environmental variables (Schmidt et al., 2011) which may vary with climate, land use and time, possibly

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transforming colluviums into C sources at a longer time scale, especially under dryer or warmer conditions.

This two stages prognostic about the fate of soil OC transferred along a hillslope corroborates the suggestions of Van Oost et al (2012): decomposition rates of buried OC can potentially increase as a result of global warming, desiccation of saturated soils, land use change, and re-excavation by gullyng, etc. The large store of buried C cannot be assumed to be inert to further loss, and indeed might become a significant C source (Van Oost et al., 2012).

Hence, the longer-term stability of these buried OC stocks in upland soils is far from certain. Given the predicted changes in climate regimes, this is a topic at which scientists and policy makers should look closely and carefully. This may challenge the current point of view considering a net terrestrial uptake of c. 1.4 Pg C yr⁻¹ (Lal 2003; Schimel et al., 2001). At least, the strength of soils as a C sink or a C source should be recalculated using models which include slope and landscape effects in their modeling concepts. Despite models uncertainties, increasing model complexity by accounting for topography effects on C dynamics seems to be a realistic way to better understand the processes responsible for net sources and sinks of carbon and to balance the global C balance with a higher level of precision (e.g. Arrouays et al., 1998; Houghton, 2007; Webster et al., 2008a).

In addition, under current environmental conditions, the respiration rates are c. 30% to c. 50% higher at the footslope. Indeed, while the CO₂ efflux is substantially suppressed by the wetter soil conditions in depositional areas, the large stock of labile OC found at the bottom of the slope results in enhanced soil respiration. This demonstrates the need to consider landscape effects when modeling and quantifying soil OC dynamics. For our study site, accounting only for soil C dynamics representative of flat landscapes would under-estimate annual soil-atmosphere CO₂ exchanges by c. 20 %.

Hence, through the different results obtained here and summarized in section 8.1, we reached the overall objective of the presented thesis, by improving

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both understanding and modeling of soil organic carbon dynamics, and quantifying CO₂ fluxes to the atmosphere at the scale of a hillslope under the pedo-climatic context of the Belgian loess belt. However, as described in the following section, some questions need to be addressed in future research.

8.3. Limitations and perspectives

8.3.2. Complete OC balance

In order to understand the impact of these findings in terms of C balance, it is important to compare these heterotrophic respiration fluxes to other soil C inputs and outputs, as illustrated on Figure 8.1. Among other things, soil heterotrophic respiration fluxes discussed here only constitute c. 30% of the total ecosystem respiration, also composed of aboveground and belowground autotrophic respiration fluxes (Suleau et al., 2011; Table 7.3) which were not considered here. In addition, these positive fluxes (from the soil to the atmosphere) are compensated by negative fluxes (CO₂ uptake from the atmosphere) through photosynthesis leading to the gross primary productivity (e.g. Ceschia et al., 2010; Kutsch et al., 2010; Moors et al., 2010). Once produced with atmospheric C, vegetal biomass can either be harvested and exported (positive fluxes), or decompose and enrich soil in new photosynthate OM (negative fluxes) (e.g. Ceschia et al., 2010; Kutsch et al., 2010; Moors et al., 2010). Manure application can also constitute a new input of OC in soils (negative flux). Hence, the actual net C balance of the soil-atmosphere system could only be assessed by considering and quantifying all these fluxes, and by comparing it to the soil heterotrophic respiration flux discussed here. However, this exceeds the scope of this study and should be explored at the scale of hillslopes in future researches.

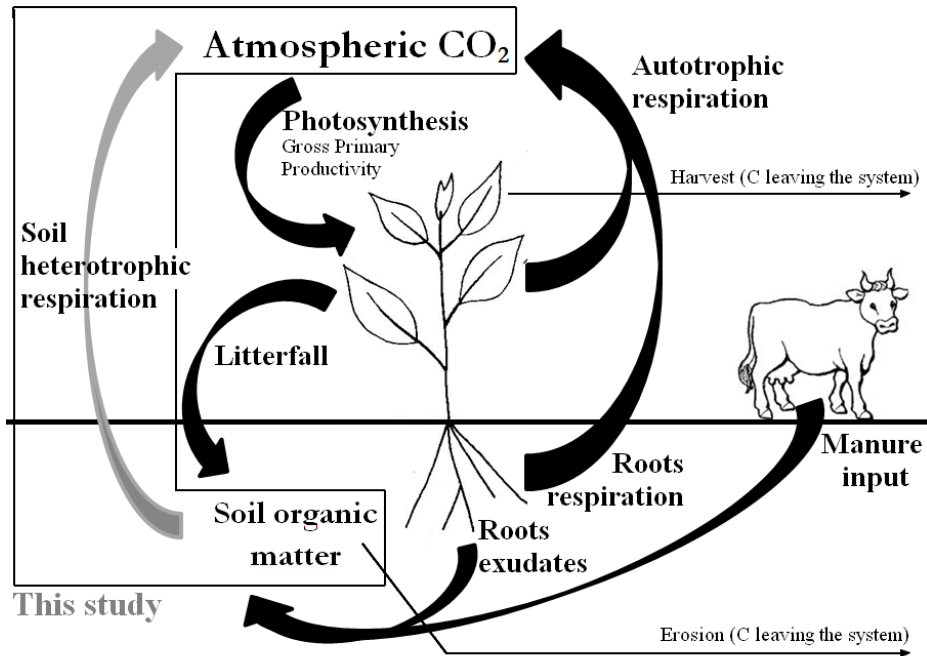


Fig. 8.2. Schematic representation of all the fluxes (inputs and outputs) contributing to the soil-atmosphere OC balance.

8.3.1. Carbonates-related CO₂ fluxes

While thermodynamic and kinetic controls of soil CO₂ fluxes related to soil alkalinity are well established (e.g. Appelo and Postma, 1994; Plummer et al., 1979), the understanding of their contribution to total soil CO₂ fluxes remains challenging, as these fluxes strongly depends on the dynamic behavior of many soil environmental factors such as soil pH, soil moisture, or the state of the soil ecosystem (closed or open). In chapter 5, we highlighted that CO₂ emissions from abiotic sources are likely interfering with respiration monitoring experiments (biotic CO₂ fluxes, chapters 4 and 7) in temperate climatic conditions. However, this would need further investigation to both proof and quantify this carbonates-related CO₂ fluxes under our pedo-climatic context.

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Hence, scope exists to elucidate the role of soil alkalinity and geochemical processes in total CO₂ emissions or uptake, particularly under temperate and continental climates, which are “end-members” climatic conditions relative to other climates under which abiotic CO₂ emissions were demonstrated (Laponis et al., 2008; Shanhun et al., 2012, 2013; Serrano-Ortiz et al., 2010; Xie et al., 2009). To that aim, in-situ experiments elucidating abiotic CO₂ emissions in temperate climate conditions would be especially needful.

Stable isotopic C signatures ($\delta^{13}\text{C}$) have been widely used to discriminate between the origin (inorganic or organic) of CO₂ fluxes in laboratory experiments (e.g. Bertrand et al., 2007). However, the results provided by stable isotopic techniques are sometimes based on weak theoretical assumptions. Hence, many challenges have to be taken up and the technologies related to stable isotopes have to be developed on the field of in-situ discrimination of biotic and abiotic CO₂ fluxes sources.

First, isotopic fractionation occurs between a substrate and a product in a given reaction (Schiavo et al., 2007; Werth and Kuzyakov, 2010; Brüggemann et al., 2011; Frisia et al., 2011). Many studies using the $\delta^{13}\text{C}$ technique do not account for this enrichment factor.

Second, CO₂ molecules with different C isotopes diffuse through soil pores at different rates and promote the enrichment of the ¹²C-CO₂ in direction of the flow (Salomons and Mook, 1976; Cerling, 1984; Cerling et al., 1991; Davidson, 1995). Despite the existence of a sound theoretical basis for this phenomenon of diffusional fractionation, its magnitude was never measured. For now, most studies dealing with the study of CO₂ emissions from soil (e.g. Biasi et al., 2008) ignore this diffusional fractionation.

Third, the $\delta^{13}\text{C}$ of soil OC is influenced by soil-forming processes and vary considerably along the soil profile (Ehleringer et al., 2000; Wynn et al., 2005; Wynn et al., 2006; Brüggemann et al., 2011). When in-situ field measurements are performed, it should be considered that the soil concentration and isotopic signature of CO₂ sampled at a given depth is, in general, the result of the

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production of CO_2 at this given depth and the vertical diffusion through soil pores of soil CO_2 produced deeper in the soil profile. Hence, the isotopic calculation methods should be adapted to account for a conceptually layered soil.

Forth, in many studies, the $\delta^{13}\text{C}$ of soil carbonate ($\delta^{13}\text{C}_{\text{CaCO}_3}$) is used as a reference (Stevenson and Verburg, 2006; Bertrand et al., 2007; Biasi et al., 2008; Tamir et al., 2011), considering that $\delta^{13}\text{C}$ of alkalinity-related CO_2 is the same than soil carbonates. However, this is not in agreement with the underlying process (e.g. Skidmore et al., 2004) explained in chapter 5, whereby abiotic CO_2 is in equilibrium with soil alkalinity and not with soil carbonates.

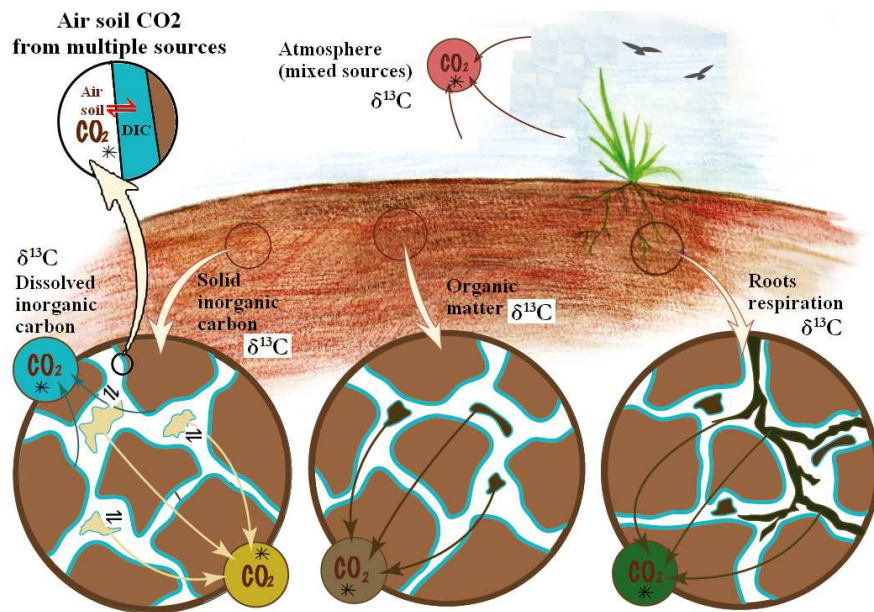


Fig. 8.2. Schematic representation the wide range of origins and ^{13}C isotopic signature of soil CO_2 . In the zoomed circles, big brown shapes represents soil grains, small dark brown shapes are organic matter particles, small beige shapes are soil carbonates (in dynamic equilibrium with dissolved inorganic carbon (DIC)), dark green line illustrate roots, and blue lines represent soil water: each of these C species are associated with CO_2 emissions with specific ^{13}C isotopic signatures ($\delta^{13}\text{C}$).

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In addition, the C contained in DIC species can originate from a wide range of different external sources with specific $\delta^{13}\text{C}$, as suggested by Telmer and Veizer (1999). These include C from atmospheric CO_2 , CO_2 produced in soils by biological activities (decomposition of organic matter, plant root respiration, etc.), CO_2 produced by soil pedogenic or loess carbonates, etc. Hence, if no direct measurements are available, an accurate estimation of the $\delta^{13}\text{C}$ of DIC remains challenging due to the varying origins and its dynamic equilibrium with other C molecules in the environment (Figure 8.2).

While further researches could focus on this topic, we could not elucidate this question in the framework of this thesis, given the series of methodological limitations that we faced, as described here above.

8.3.2. Further improvement in soil OC dynamics modeling

Current approaches for quantifying OC turnover in soils are typically informed by 1-D vertical modelling concepts that focus on the understanding of soil OC turnover in flat, non-sloping landscapes. In an effort to address this shortcoming, we tried to account for spatially dynamic processes by comparing different positions along a hillslope, whereby we separately modeled and studied the different slope positions through a 1-D vertical model approach. It is clear that a next logical step is the development of fully spatially explicit models where the hillslope is represented by a set of connected profiles that interact through lateral processes.

In addition, we considered the hillslope as a transect without any spatial variability in the lateral dimension (along level curves). Hence, 2-D or even 3-D OC dynamics models should be developed that account for the same mechanistic concepts with the same precision than performing 1-D model (as SOILCO₂-RothC used in this study). This could be done by coupling OC dynamics models (like RothC) with 2-D or 3-D or spatialized hydrodynamic models (e.g. Hydrus; or Wave, Vanclooster et al., 1994). To account for lateral transfer of

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sediments and soil OC, these should also be coupled with a geomorphological model as SPEROS-C (e.g. Van Oost et al., 2005).

Using the 1-D SOILCO₂-RothC model, scope exists for future work to provide site-specific characterization of some parameters, completing the work of Bauer et al. (2011) and Herbst et al. (2008). This would however need longer time-series observations to calibrate and validate the model (e.g. 8 full years in Herbst et al., 2008).

8.3.3. Spatial generalization

Based on the mechanistic understanding of the processes presented in this thesis, future researches should try to validate their occurrence in other sites and/or at larger spatial scales inside the loess belt. This validation strategy could be based on a widespread measurements network. This could also be done using technologies directly allowing to measure CO₂ fluxes at larger scale, i.e. Eddy covariance towers. The use of this technique would however need some methodological adaptations to circumvent the sloping feature of the studied areas which are known to bias the results of Eddy covariance measurements (e.g. Baldochi, 2003).

Under other pedo-climatic areas, however, we do not expect similar behavior of soils in terms of soil OC persistence. For instance, we showed in this thesis the importance of the soil physical and hydrological control on soil-atmosphere C exchanges. Hence, under drier climates, or in soils with a higher drainage, downslope erosion-induced deposits are not expected to store important amount of soil OC, as these OC deposits should be mineralized more directly and progressively than in colluviums of temperate climates. As a second example, the quality of the soil OC at the different positions along the hillslope is dependent on the soil types and their content in reactive mineral phases. Another pedological and geomorphological context would completely alter this OC quality distribution (chapter 3) and the consequent potential of stability of soil OC.

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