Hydrologic Mediation of the Spatial and Temporal Variability of the Soil Carbon Dioxide Stable Isotopic Composition of a Subalpine Watershed

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HYDROLOGIC MEDIATION OF THE SPATIAL AND TEMPORAL VARIABILITY
OF THE SOIL CARBON DIOXIDE STABLE ISOTOPIC COMPOSITION OF A
SUBALPINE WATERSHED

by

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HYDROLOGIC MEDIATION OF THE SPATIAL AND TEMPORAL VARIABILITY OF THE SOIL CARBON DIOXIDE STABLE ISOTOPIC COMPOSITION OF A SUBALPINE WATERSHED

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The stable carbon isotopic composition of CO$_2$ ($\delta^{13}$C-CO$_2$) has been studied as an indicator of changes in ecosystem CO$_2$ exchange. Soil moisture is an important factor in ecosystem CO$_2$ exchange through its influence on physiological and soil physical processes. However, the majority of previous research analyzing the influence of soil moisture on soil and soil-respired $\delta^{13}$C-CO$_2$ has been conducted with limited consideration of topographical variation, which controls the distribution of soil moisture across a landscape. This study characterized the stable isotopic composition ($\delta^{13}$C) and concentrations of soil CO$_2$ at 5, 20, and 50 cm across seven transects in two subalpine watersheds in the Tenderfoot Creek Experimental Forest, Montana. The results show that soil $\delta^{13}$C-CO$_2$ varies systematically with topography and soil moisture gradients. In response to a soil moisture drydown, bulk soil $\delta^{13}$C-CO$_2$ and the calculated $\delta^{13}$C-CO$_2$ value of the biological source in upland areas became more positive. This is consistent with an increase in plant $\delta^{13}$C-CO$_2$ with drought stress due to a decrease in photosynthetic discrimination, and has been observed previously at smaller scales. In contrast, soil $\delta^{13}$C-CO$_2$ did not change significantly in riparian areas, where soil moisture remained high.
throughout the field season. Elevation was positively correlated with soil $\delta^{13}$C-CO$_2$, following the negative gradient of soil moisture and atmospheric pressure with increasing elevation. Elevation and soil moisture were significantly correlated for two-thirds of the growing season when soil moisture was at medium-high levels, and elevation was a positive predictor of bulk soil $\delta^{13}$C-CO$_2$ during the same time period. Plot soil moisture measurements were better predictors of soil CO$_2$ concentration and soil CO$_2$ flux than topographical attributes. This study indicates that in complex terrain at high to medium soil moisture levels, the variability of soil $\delta^{13}$C-CO$_2$ is systematically linked to landscape position, possibly largely due to the influence of topographical heterogeneity on soil moisture distribution.
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CHAPTER 1: INTRODUCTION

SUMMARY

The hydrological cycle plays a large role in the expression of different terrestrial ecosystem processes. Climate change is expected to intensify the hydrologic cycle (IPCC 2007), and as a result it is important to characterize how terrestrial ecosystem processes will respond to changes in hydrologic forcings. Terrestrial ecosystems are large carbon reservoirs, and the hydrological cycle mediates multiple physical and biological processes that modulate ecosystem carbon storage. Of the many important terrestrial ecosystem processes is soil carbon efflux, which is a large part of the natural efflux of CO$_2$ to the atmosphere.

Stable carbon isotope analysis has been used to identify and quantify the physical and biological mechanisms of soil CO$_2$ respiration. Isotopic discrimination in plants as a result of photosynthesis and post-photosynthetic transport is reflected in the stable carbon isotopic composition of soil. Similarly, the physical process of diffusion affects soil stable carbon isotopic composition through the preferential diffusion of $^{12}$C-CO$_2$ within the soil column as well as diffusion of atmospheric CO$_2$ into the soil. Soil moisture variation impacts both the physical and biological processes that determine the stable carbon isotopic composition of soil CO$_2$ respiration.

In mountainous landscapes, topography is an important driver of the lateral redistribution of soil water, which drives the spatial distribution of soil water content. As
soil water affects the physical and biological mechanisms of soil CO₂ efflux, the examination of the effect of topography on soil CO₂ efflux through soil moisture distribution is needed in order to fully understand the dynamics of soil CO₂ efflux in mountainous landscapes. A majority of the previous work analyzing the influence of hydrology on soil and soil-respired δ¹³C-CO₂ has focused on plots or areas with small topographic variability, not taking the full spatial variation of complex terrain into account. This thesis addresses the role of topography in influencing soil and soil-respired δ¹³C-CO₂ across a whole watershed through soil moisture variation and contributes to the further understanding of the linkage between topography, hydrology, and terrestrial carbon processes.

INTRODUCTION

Hydrology underpins many of the Earth’s terrestrial nutrient and elemental processes. Any changes in hydrological patterns will thus result in corresponding shifts in these different processes. Climate change is expected to increase the variability of the hydrologic cycle from the local to the global scales (IPCC 2007); therefore it is important to characterize the interaction of the water cycle with different terrestrial ecosystem processes to quantify how these processes will vary with climate change.

The hydrological cycle is directly connected to terrestrial ecosystems through soil moisture (National Research Council, 2012). The interaction and feedback between the two are critical as the terrestrial ecosystem is one of the earth’s largest carbon reservoirs. Carbon is stored in the long-term pools of soil organic matter and vegetation and fluxes
continually between these pools and to other reservoirs such as the atmosphere and the ocean. As such, terrestrial ecosystems constitute approximately 76% of the total carbon flux to and from the atmosphere, in the form of plant photosynthesis and respiration from both vegetation and soil. The latter contributes around 37% of the total flux through decomposition processes (Houghton, 2007).

Soil moisture is one of the main drivers of soil CO$_2$ respiration through the stimulation of biotic activity, and the variability of soil CO$_2$ is known to correspond to the spatial and temporal variability of soil moisture (Kowalenko et al., 1978; Singh & Gupta, 1977). As such, one of the current research challenges in the study of the interaction of soil moisture with CO$_2$ respiration is moving from the examination of their dynamics at small scales such as a single leaf or a soil plot to larger spatial scales (Katul, et al., 2007; Vargas et al., 2010). In complex terrain, topographical variability systematically influences the distribution of soil water and so the variability of soil CO$_2$ respiration (Pacific et. al, 2011). Linking topography and the variation of physical and biological mechanisms of soil CO$_2$ is essential for the analysis of soil CO$_2$ dynamics beyond small-scale plots.

**BIOLOGICAL AND PHYSICAL FACTORS AFFECTING SOIL CO$_2$ AND SOIL CO$_2$ EFFLUX**

The biological production of soil CO$_2$ can be divided into two main components: autotrophic and heterotrophic respiration (Raich & Nadelhoffer, 1989). The autotrophic component is composed of root respiration, surface litter decomposition, and oxidation of
soil organic matter (Ehleringer et. al, 2000; Mishra & Riley, 2012), while the heterotrophic component is made up of CO\textsubscript{2} respired by soil bacteria, fungi, and fauna (Anderson, 1982; Singh & Shukla, 1977). Both components can in turn be affected by an increase in soil temperature which can stimulate plant and heterotrophic metabolism, resulting in higher CO\textsubscript{2} respiration rates (Singh & Gupta, 1977; Witkamp, 1969).

The main physical factor that affects soil CO\textsubscript{2} respiration is gas diffusivity, which is in turn affected by soil texture, soil bulk density, and soil moisture (Penman, 1940; Rolston & Moldrup, 2002). Soils with high bulk density generally have low soil CO\textsubscript{2} efflux due to reduced gas diffusivity (Novara et al. 2012). The same researchers observed that soil CO\textsubscript{2} efflux is higher from fine textured soils since they can hold more water and so are more favorable for microbial activity. Conversely, saturation conditions found in soils which have a soil moisture higher than the optimal range can impede soil CO\textsubscript{2} diffusivity, resulting in decreased soil CO\textsubscript{2} efflux (Davidson et al., 2000).

Experiments that examine how soil moisture variability affects soil CO\textsubscript{2} dynamics have mostly focused on the effect of these changes on its biological determinants. The amount of heterotrophic CO\textsubscript{2} respiration after a precipitation pulse can be affected by the interaction of soil moisture, soil temperature, and labile C availability (Berryman et. al, 2012). Rain increases microbial activity due to the breakdown of soil aggregates by water, resulting in greater labile organic C availability (Novara et al., 2012). In contrast, drought results in decreased heterotrophic litter decomposition and both heterotrophic
and autotrophic respiration, and therefore less soil CO₂ efflux (Allison et al., 2013; Joos et al., 2010).

An optimal range of soil moisture for maximum soil CO₂ efflux exists. When soil moisture is low, autotrophic and heterotrophic CO₂ production decreases (Wildung et. al, Epron). However, when soils are oversaturated, both gas diffusivity and CO₂ production are impeded (Davidson & Trumbore, 1995; Linn & Doran, 1984). The range of optimal soil moisture for CO₂ efflux is usually found around the field capacity value of a soil (Linn & Doran, 1984).

Soil CO₂ efflux also changes in response to the temporal variability of soil moisture. At the diel timescale, soil moisture can affect the relationship of soil CO₂ efflux with changes in soil temperature (Riveros-Iregui et. al, 2007). On a seasonal timescale, soil moisture is strongly influenced by precipitation inputs, and so precipitation variability affects the seasonal variability of soil CO₂ efflux (Harper et. al, 2005; Knapp et al., 2002). In a snow-dominated mountain ecosystem, Moyes & Bowling (2012) found that seasonal precipitation variability affected soil CO₂ production and efflux through its influence on different soil mechanisms throughout the period of the study. In the same study, vegetation growth after snowmelt and modeled soil CO₂ production and efflux peaked at the same time, while during late summer and early fall, an increase in soil CO₂ production and efflux was attributed to rain-induced spikes in heterotrophic respiration. The same study also found that temperature affects seasonal variability, as increased soil CO₂ efflux that corresponded to summer temperature increases was attributed to
enhanced autotrophic and heterotrophic metabolism. The effect of temperature on soil CO$_2$ efflux, however, is also mediated by soil moisture (Riveros-Iregui et al., 2007). As a whole, seasonal CO$_2$ efflux variability depends on changing relationships between soil moisture, temperature, and substrate availability for roots and soil microorganisms (Reichstein et al., 2003; Wang, et al., 2003). Seasonal leaf litter decomposition, which is highly responsive to soil moisture variation, can act as a major contributor to heterotrophic CO$_2$ respiration, whereas root respiration was found to remain constant throughout the seasons (Cisneros-Dozal et. al, 2006).

**STABLE CARBON ISOTOPE ANALYSIS**

The dynamics of different processes involved in soil CO$_2$ and soil CO$_2$ respiration can be examined through the analysis of the spatial and temporal variation of their stable carbon isotope composition. Stable isotope $^{13}$C values are often reported using the delta notation (1), which measures the deviation of the ratio of $^{13}$C and $^{12}$C in a sample from that present in the international standard of Vienna Pee Dee Belemnite (VPDB)(Craig 1957; Farquhar et al. 1989).

$$\delta_p = \frac{R_p - R_s}{R_s} = \frac{R_p}{R_s} - 1$$

(1)

where $R_p = ^{13}$C/$^{12}$C of sample and $R_s = ^{13}$C/$^{12}$C of VPDB. The delta notation of the sample, $\delta_p$, is reported in units of per mille (‰).
BIOLOGICAL AND PHYSICAL FACTORS AFFECTING SOIL AND SOIL-RESPIRE \( \delta^{13} \)C-CO\(_2\) COMPOSITION

Figure 1.1 Average \( \delta^{13} \)C-CO\(_2\) of CO\(_2\) pools associated with soil CO\(_2\) efflux. (Gillon et al., 2012)

The average soil \( \delta^{13} \)C-CO\(_2\) in a given area is expected to be similar to that of the area’s vegetation, which is the primary source of soil carbon (Amundson et. al, 1998). Farquhar et al. (1989) enumerated the different photosynthetic processes and locations where plants actively discriminate against \( ^{13} \)C-CO\(_2\). In plants which have a C\(_3\) photosynthetic pathway, the most significant process where discrimination occurs is the fixation of CO\(_2\) by the enzyme of Rubisco in leaves, which results in a leaf \( \delta^{13} \)C-CO\(_2\) value of -30 to -24 ‰ (Figure 1). This leaf \( \delta^{13} \)C-CO\(_2\) discrimination is reflected in the
\(\delta^{13}C\)-CO\(_2\) of root respiration, and therefore ultimately in the CO\(_2\) efflux from the soil (Brüggemann et al., 2011; Ekblad & Högberg, 2001).

As with the magnitude of soil CO\(_2\) efflux, soil moisture variability affects the isotopic composition of soil CO\(_2\) efflux (Bowling et al., 2008; Ekblad & Högberg, 2001). Under drought conditions, the intercellular partial pressure of CO\(_2\) within a leaf decreases and the stomata respond to the steeper soil water potential gradient by closing slightly (Burrows & Milthorpe, 1976; Dawson & Ehleringer, 1998; Farquhar, et. al, 1989). These changes within the leaf can be measured as an increase in the leaf’s \(\delta^{13}C\) value (Farquhar et al. 1989), and as mentioned previously, will be reflected in the \(\delta^{13}C\)-CO\(_2\) of soil CO\(_2\) efflux.
Figure 1.2. Estimates of apparent fractionation associated with soil microbial respiration determined by different experimental approaches (gray: C$_3$ plants; dark gray: Rayleigh distillation, black: C$_4$ plants). The dashed line is the mean of all estimates. (Brüggemann et al., 2011)

Compared to autotrophic isotopic discrimination, the contribution of heterotrophic discrimination to the biological $\delta^{13}$C-CO$_2$ signature of soil and soil-respired CO$_2$ is minor, as the degree of estimated microbial isotopic discrimination is much less than values of leaf discrimination (Brüggemann et al., 2011; Werth & Kuzyakov, 2010). As shown in Figure 2, the majority of the soil microbial isotopic fractionation values that have been estimated in soils with C$_3$ vegetation lie between -1 and 1.5 ‰. Although experiments have yielded a wide range of microbial fractionation estimates for different photosynthetic pathways (Figure 2), it remains to be determined if these results can be solely attributed to microbial fractionation or if they have been confounded by
differences in soil substrates or microbial community composition (Brüggemann et al., 2011). Although theory suggests that isotopic fractionation might be present in some microbial respiration processes, a link between a specific biochemical process and direct isotopic fractionation has not yet been shown (Bowling et al., 2008). While there are some studies that posit that the $\delta^{13}C$ of heterotrophic respiration can vary depending on moisture and substrate availability (Joos et al, 2010; Kodama et. al, 2008; Salmon et. al, 2011), field experiments have shown that carbon stable isotope discrimination is not observed in heterotrophic respiration, even along moisture gradients (Phillips et al., 2010; Risk et al., 2012; Tiunov, 2007).

As the biological source of soil $\delta^{13}C$-CO$_2$ (also called the $\delta^{13}C$-CO$_2$ of production or $\delta_j$) is difficult to measure directly, it is often estimated from mixing models that use soil bulk $\delta^{13}C$-CO$_2$ measurements. One that is most commonly used is the Keeling plot method, derived by Keeling (1958). It is a two-component linear mixing model with the isotope ratio of atmospheric CO$_2$ and the isotope ratio of the CO$_2$ source as its end members:

$$\delta_s = C_a (\delta_a - \delta_j) / (1/C_s) + \delta_s \quad (2)$$

where $\delta_s$ is the isotope ratio of the total CO$_2$ mixing ratio, $\delta_a$ is the isotope ratio of atmospheric CO$_2$, and $\delta_s$ is the isotopic ratio of the CO$_2$ source. Davidson (1995) described a complementary model where production can be calculated using the following equation:
\[ \delta_j = \frac{C_s(\delta_s - 4.4) - C_a(\delta_a - 4.4)}{1.0044(C_s - C_a)} \% \]  
(3)

where \( \delta_j \) is the isotopic ratio of the CO\(_2\) source, \( \delta_a \) is the isotopic ratio of atmospheric CO\(_2\), \( C_a \) is the atmospheric CO\(_2\) concentration, \( \delta_s \) is the isotopic ratio of the soil gas, and \( C_s \) is the corresponding CO\(_2\) concentration of soil gas. In contrast with the Keeling plot, where the isotopic ratio of soil CO\(_2\) production is estimated using measurements, only two points are needed for the Davidson-derived equation: an atmosphere measurement and a soil gas measurement.

At depth, the gradient of soil isotopic composition has been shown to be a function of mixing between the isotopic signature of the CO\(_2\) source and that of the atmosphere, as well as the respiration rate of the soil (Cerling et. al, 1991; Cerling, 1984). Physical diffusion can mainly impact the \( \delta^{13}\text{C}-\text{CO}_2 \) gradient of soil in two ways: through preferential molecular diffusion of \(^{12}\text{C}\) upwards through the soil column and the diffusion of atmospheric air which is enriched in \( \delta^{13}\text{C}-\text{CO}_2 \) downwards through the soil column. The \( \delta^{13}\text{C}-\text{CO}_2 \) of soil CO\(_2\) is at least 4.4\% more enriched than that of soil-respired CO\(_2\) because of preferential molecular diffusion (Cerling et. al, 1991).

Aside from the source of carbon isotope discrimination and mixing in the soil column, one of the important factors that need to be considered when looking at ecosystem carbon isotopic composition variability is the difference in turnover time between carbon pools and fluxes. Fessenden & Ehleringer (2003) determined that both soil and ecosystem-respired CO\(_2\) varied through time with soil moisture levels, with
variations three times that of the carbon stocks of needles and soil organic carbon. Thus, carbon stocks integrate isotopic discrimination for a longer time than carbon fluxes, which can respond more quickly to changes in moisture. In addition to leaf organic matter, the δ¹³C-CO₂ of soil CO₂ respiration may also be linked to more short-term meteorological changes such as precipitation, vapor pressure deficit, and soil drought (Werner et al. 2006).

SOIL CO₂ RESPIRATION AND SOIL δ¹³C-CO₂ AT THE LANDSCAPE SCALE

Landscape factors such as slope, elevation and catchment morphology affect the spatial variability of both soil CO₂ respiration and soil moisture (Brocca et al., 2007; Chen et al., 2005; Pacific et al., 2008). Elevation gradients can exhibit corresponding changes in carbon processes- snow accumulation has a positive effect on photosynthetic activity at middle elevations, with a reduced effect at energy-limited higher elevations (Trujillo et al., 2012). Overall, the interaction of vegetation and topography with climate factors determined whether certain zones in a complex landscape were perpetual carbon sinks, sources, or switched between the two (Emanuel et al., 2011). As topographical variability determines the direction and magnitude of soil water distribution in a complex landscape, different areas of the landscape will respond differently to temporal precipitation changes (Riveros-Iregui et al., 2012). These differences in water availability will correspond to variability in solutes that are in the soil water, as well as biological and physical processes that depend on soil water.

As with soil water, soil CO₂ efflux has also been shown to vary in accordance with landscape position. The main drivers of soil CO₂ respiration include soil moisture, soil temperature, soil substrate, root biomass, vegetation type (Singh & Gupta, 1977), and
so the systematic arrangement of these as determined by topography can result in the corresponding arrangement of soil CO₂ respiration. Pacific et al. (2011) determined that soil CO₂ efflux was consistently higher in riparian areas compared to adjacent hillslopes because of a wider range in soil moisture, variable groundwater table position, and optimal C:N ratios. Soil CO₂ efflux in dissimilar areas of a landscape can respond differently to temporal hydrologic variability. In a wet year with higher soil moisture than the average, researchers observed a decrease in soil CO₂ efflux in riparian areas (Pacific et al., 2009). This was attributed to an extended period of time where the soil moisture was higher than the optimal soil moisture levels, inhibiting gas transport and production. In contrast, soil CO₂ efflux in the hillslope upland areas adjacent to the riparian areas increased in the same wet year. When soil CO₂ efflux and soil moisture were measured over a larger area in the same watershed, the response of soil CO₂ efflux to temporal hydrologic variability was shown to be a continuous function of the drainage area at a particular location of the watershed (Riveros-Iregui et al., 2012).

Researchers have examined whether the relationships between δ¹³C and environmental variables at a site or plot level also apply to larger scales. Across a watershed, the variability of the δ¹³C-CO₂ of different components of ecosystem respiration corresponded to precipitation patterns and hydrologic variability (Riveros-Iregui et al., 2011). The same study also examined whether patterns of leaf δ¹³C-CO₂ were transferable to the δ¹³C-CO₂ of ecosystem respiration. It was found that leaf δ¹³C-CO₂ can indeed be indicative of the δ¹³C-CO₂ of ecosystem respiration, but only under dry climatic conditions.
TOPOGRAPHICAL CONSIDERATIONS IN CURRENT SOIL AND SOIL-RESPIRED CO$_2$/δ$^{13}$C-CO$_2$ RESEARCH

Most of the research looking at the variability of soil CO$_2$ efflux and soil δ$^{13}$C-CO$_2$ in terrestrial landscapes as well as their connection with soil moisture has been conducted either without or with limited consideration of topographical variation. Greenhouse and incubation experiments have allowed researchers to observe how the manipulation of environmental factors, such as soil moisture, affects soil δ$^{13}$C-CO$_2$ (Phillips et al., 2010). Soil CO$_2$ production and concentrations, soil δ$^{13}$C-CO$_2$, and environmental factors in the soil profile has also been studied in the field through the installation of continuous measurement soil CO$_2$ probes and portable analyzers such as Tunable Diode Laser Absorption Spectrometers (Goffin et al., 2014). However, the spatial scale of these intensive studies has often been limited to selected points or a few plots. At these small spatial scales, soil and soil-respired CO$_2$ and δ$^{13}$C-CO$_2$ have been found to vary in response to changes in soil moisture, through both simulated (simulated precipitation, water pulses, etc.) and natural events (natural precipitation, gradual seasonal drydown, etc.).

Field research on the effect of soil moisture variability on soil and soil-respired CO$_2$ and δ$^{13}$C-CO$_2$ at scales larger than individual sites has incorporated topographical variation in terms of altitude gradients or the comparison of different land use and landscape types (Davidson et al., 2000; Wang et al., 2010). Acosta et al., (2013) conducted extensive soil δ$^{13}$C-CO$_2$ sampling of different landscapes, but measurements were not taken simultaneously, and the period of measurement was limited to only 5 days. Studies have also looked at the variability of soil δ$^{13}$C-CO$_2$ at different altitudes,
but have focused on the importance of vegetation and not other environmental factors (Bird et al., 1994; Chen et al., 2005). Pacific et al. (2009) established that the soil CO₂ efflux in riparian areas and their adjacent hillslopes had opposite reactions to temporal soil moisture variation. When the scope of the previous study was expanded by Riveros-Iregui et al. (2012) to include a whole sub-watershed, the response of soil CO₂ efflux to temporal soil moisture variation was determined to be a continuous function of the drainage area at a particular measurement location. The influence of landscape structure on soil and soil-respired δ¹³C-CO₂ variability has not yet been determined.

**THESIS OBJECTIVES**

This thesis addresses the role of topography in influencing soil and soil-respired δ¹³C-CO₂ across complex terrain through soil moisture variation. There are three objectives, namely:

1) To characterize the spatial variability of soil CO₂ (δ¹³C-CO₂, concentration, and flux) at the scale of a single watershed in response to topographic variability.

2) To examine the response of soil CO₂ to seasonal changes in soil moisture availability across at the scale of a single watershed.

3) To examine the spatial and temporal variability of soil CO₂ at different levels and landscape positions of a single watershed.

The next chapter presents measurements of soil δ¹³C-CO₂ and the calculated δ¹³C-CO₂ of soil respiration taken throughout a complex watershed and links them with landscape position through soil moisture. In a complex landscape where the main
precipitation input is snow, the seasonal drydown corresponding with the growing season results in high spatial and temporal soil moisture variability. This hydrologic variability was in turn systematically reflected in the spatial and temporal variation of the soil $\delta^{13}$C-CO$_2$ across the landscape.

A majority of previous experimental work analyzing the influence of soil moisture on soil and soil-respired $\delta^{13}$C-CO$_2$ has focused on plots or areas with small topographical variability, and therefore not taken the full spatial variation of complex terrain into account. Through the examination of soil and soil-respired $\delta^{13}$C-CO$_2$ in a complex landscape by manual measurements of soil gas wells across a large number of sites with varying landscape positions, this thesis contributes to the further understanding of the linkage between terrestrial carbon processes and hydrology.
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CHAPTER 2: THE HYDROLOGICAL MEDIATION OF SOIL $\delta^{13}$C-CO$_2$ IN A COMPLEX LANDSCAPE

INTRODUCTION

Hydrology underpins many of the Earth’s terrestrial nutrient and elemental processes. Any changes in hydrological patterns will thus result in corresponding shifts in these different processes. Climate change is expected to increase the variability of the hydrologic cycle from the local to the global scales (IPCC 2007); therefore it is important to characterize the interaction of the water cycle with different terrestrial ecosystem processes to quantify how these processes will vary with climate change.

The hydrological cycle is directly connected to terrestrial ecosystems through soil moisture (National Research Council, 2012). The interaction and feedback between the two are critical as the terrestrial ecosystem is one of the earth’s largest carbon reservoirs. Carbon is stored in the long-term pools of soil organic matter and vegetation and fluxes continually between these pools and other reservoirs such as the atmosphere and the ocean. Terrestrial ecosystems account for around 76% of the total carbon flux to and from the atmosphere, in the form of plant photosynthesis and respiration from both vegetation and soil. The latter contributes around 37% of the total flux through decomposition processes (Houghton, 2007). The accuracy of the estimated CO$_2$ budgets of CO$_2$ reservoirs can be improved through the coupling of CO$_2$ stable isotope measurements with CO$_2$ flux measurements (Tans, et al., 1993; Wittenberg & Esser, 1997). The dynamics of different processes involved in terrestrial CO$_2$ respiration can be
examined using the spatial and temporal variation of the stable carbon isotope composition of ecosystem CO$_2$ respiration components, which are reported using the delta notation, $\delta_p$ (where $p$ is the sample value).

Soil $^{13}$C-CO$_2$ composition is determined by biological production as well as physical processes such as diffusion. At depth, the gradient of soil $^{13}$C-CO$_2$ composition has been shown to be a function of mixing between the isotopic signature of the CO$_2$ source and that of the atmosphere, as well as the respiration rate of the soil (Cerling et al., 1991; Cerling, 1984). Physical diffusion can mainly impact the $\delta^{13}$C-CO$_2$ gradient of soil in two ways: through preferential molecular diffusion of $^{12}$C upwards through the soil column and the diffusion of atmospheric air, which is enriched in $\delta^{13}$C-CO$_2$ downwards through the soil column. The $\delta^{13}$C-CO$_2$ of soil CO$_2$ is at least 4.4‰ more enriched than that of soil-respired CO$_2$ because of preferential molecular diffusion (Cerling et al., 1991).

The carbon isotopic composition of the soil is expected to be highly similar to that of plants because plants are the primary source for soil carbon (Amundson et al., 1998). During CO$_2$ uptake in photosynthesis, plants discriminate against $^{13}$C, most significantly in the leaf (Farquhar et al., 1989). This leaf $\delta^{13}$C-CO$_2$ discrimination is reflected in the $\delta^{13}$C-CO$_2$ of root respiration, and therefore ultimately in the CO$_2$ efflux from the soil (Brüggemann et al., 2011; Ekblad & Högberg, 2001). Compared to autotrophic isotopic discrimination, the contribution of heterotrophic discrimination to the biological $\delta^{13}$C-CO$_2$ signature of soil and soil-respired CO$_2$ is minor, as the degree of
estimated microbial isotopic discrimination is much less than values of leaf
discrimination (Brüggemann et al., 2011; Werth & Kuzyakov, 2010). Although theory
suggests that isotopic fractionation might be present in some microbial respiration
processes, a link between a specific biochemical process and direct isotopic fractionation
has not yet been shown (Bowling et al., 2008).

Soil moisture variability affects the isotopic composition of soil CO₂ efflux
through its effect on biological processes (Bowling et al., 2008; Ekblad & Högberg,
2001). Differences in soil moisture can result in changes in plant ¹³C uptake during
photosynthesis, and so in the ¹³C-CO₂ composition of soil. Under drought conditions, the
intercellular partial pressure of CO₂ within a leaf increases and the stomata respond to the
steeper soil water potential gradient by closing slightly. These processes within the leaf
can be measured as an increase in the leaf’s δ¹³C value (Farquhar et al. 1989). This
difference in leaf δ¹³C discrimination as a result of soil moisture variability is reflected in
the plant’s respiration of CO₂ through its roots into the soil, and therefore ultimately in
the CO₂ efflux from the soil (Brüggemann et al., 2011; Ekblad & Högberg, 2001).

One of the current challenges in our understanding of the interaction of the
hydrological cycle with ecosystem processes is moving from small scales such as a single
leaf or a soil plot to looking at the characteristics of these processes over large spatial
scales and complex landscapes (Katul et al., 2007; Vargas et al., 2010). Landscape factors
such as slope, elevation and catchment morphology affect the spatial variability of both
soil CO₂ respiration and soil moisture (Brocca et al., 2007; Chen et al., 2005; Pacific et
al., 2008). Topography is a strong control on hydrologic flow, and so determines the distribution of soil moisture, nutrients such as nitrogen and phosphorus, soil organic matter, and dissolved organic carbon (Creed & Sass, 2011). These differences in water availability will correspond to variability in solutes that are in the soil water, as well as biological and physical processes that depend on soil water.

Most of the research looking at the variability of soil CO$_2$ efflux and soil $\delta^{13}$C-CO$_2$ in terrestrial landscapes as well as their connection with soil moisture has been conducted either without or with limited consideration of topographical variation. Greenhouse experiments have allowed researchers to manipulate environmental factors, such as soil moisture, and monitor their effect on soil $\delta^{13}$C-CO$_2$ (Phillips et al., 2010). The profile of soil $\delta^{13}$C-CO$_2$ has also been studied in the field through the installation of continuous measurement soil CO$_2$ probes and portable analyzers (Goffin et al., 2014). However, the spatial scale of these intensive studies has often been limited to selected points or a few plots. At these small scales, soil and soil-respired CO$_2$ and $\delta^{13}$C-CO$_2$ have been found to vary in response to changes in soil moisture, through both simulated (simulated precipitation, water pulses, etc.) and natural events (natural precipitation, gradual seasonal drydown, etc.). Field research on the effect of soil moisture variability on soil and soil-respired CO$_2$ and $\delta^{13}$C-CO$_2$ at scales larger than individual sites have incorporated topographical variation through comparisons of sites at different altitude gradients or sites located in different land use and landscape types (Acosta et al., 2013; Davidson et. al, 2000; Wang et al., 2010). The influence of landscape structure on soil and soil-respired $\delta^{13}$C-CO$_2$ variability is an area of active study.
This study aims to address the role of topography in influencing soil CO$_2$ and soil and soil-respired $\delta^{13}$C-CO$_2$ across a whole watershed through soil moisture variation. Previous studies have demonstrated that soil CO$_2$ respiration is dependent on landscape position and is a function of drainage area (Pacific, et al., 2009; Riveros-Iregui et al., 2012). However, the majority of the previous work analyzing the influence of soil moisture on soil and soil-respired $\delta^{13}$C-CO$_2$ has focused on comparisons of plots or areas with small topographic variability, and has not taken the full spatial variation of complex terrain into account (Acosta et al., 2013; Davidson et. al, 2000; Wang et al., 2010). In this chapter, I present soil and soil-respired CO$_2$ and $\delta^{13}$C-CO$_2$ data collected from gas wells installed at 39 different sites across a subalpine watershed over a whole growing season. Soil moisture and soil temperature were collected concurrently with gas samples at each plot. This allows the calculation of the components of soil $\delta^{13}$C-CO$_2$ and the analysis of the spatio-temporal variability of soil $\delta^{13}$C-CO$_2$ at different scales, from plots to aggregate landscape positions (riparian and upland). I hypothesize that the spatial and temporal variability of soil and soil-respired $\delta^{13}$C-CO$_2$ is dependent on landscape position, mainly due to the topographical mediation of soil water content. The results of this study will contribute to the further understanding of the influence of soil moisture on soil respiration at the landscape scale and the linkage of terrestrial carbon processes and hydrology.

**METHODODOLOGY**

**Field Site**

The study site for the project was the subalpine Tenderfoot Creek Experimental Forest (TCEF) located at the headwaters of Tenderfoot Creek in the Little Belt Mountains
of Central Montana. The 3,591 ha site has an elevation range of 1,838 to 2,421 m (average is 2,206 m) and receives an average 890 mm of precipitation annually, ranging from 595 mm at lower elevations to 1050 mm at its upper slopes (Farnes et al., 1999). Its hydrological processes are mainly snowmelt-driven, with snow accounting for 70% of total precipitation (McCaughey, 1996). McCaughey (1996) described the normal seasonal variability of the hydrological processes in the experimental forest. Precipitation in the form of snow reaches its maximum during the month of December or January. Peak streamflow, usually observed in late May or early June, is also snowmelt-driven. Soils are at field capacity during early spring (McCaughey, 1996), and vegetation at lower elevations and on the dry south slopes of the experimental forest experience soil moisture stress through mid-July. The optimal soil moisture range for soil CO₂ production in TCEF is 40%-60% (Pacific et. al, 2008), and maximum soil CO₂ concentrations are expected to occur above 20 cm.

The vegetation in TCEF consists of C3 plants, including lodgepole pine (*Pinus contorta*), spruce (*Picea eglemanni*), whitebark pine (*Pinus albicaulis*), subalpine fir (*Abies lasiocarpa*), and grouse whortleberry (*Vaccinium scoparium*) at the upland levels and blue joint reed grass (*Calamagrostis canadensis*) in riparian areas. The most dominant soil groups are loamy, skeletal, mixed Typic Cryochrepts in upland areas and highly organic, clayey, mixed Aquic Cryoboralfs in the riparian areas. Thus, soils across the landscape range from well drained to poorly drained. The soil bulk density of riparian zones is 0.962 g cm⁻³, while that of the adjacent hillslopes is 0.911 g cm⁻³ (Pacific et al., 2011). There was no significant difference between either the soil bulk density or root density of riparian areas and the adjacent upland areas.
Field Sampling

A network of gas well plots exists along multiple transects in the field site (Pacific et al., 2008, 2011). Seven transects in total were selected to cover different topographical gradients across two subcatchments of the experimental watershed, and consisted of plots in riparian and upland areas. Four transects were located in the upland area of the Upper Stringer Creek Watershed. Of these, two transects (named NWC and NWD) were situated at the highest point of the watershed and two (SW and WH) were positioned lower on the southwest and west sides of the watershed, respectively. One upland transect (SPC) was located in the Spring Park watershed, spanning a level area that had been previously clear-cut. In this transect, plots were located in previously clear-cut areas, a transition area, and a forested area that had not been clear-cut. The remaining two transects (T1 and T2) both spanned riparian-upland transition areas in the Upper Stringer Creek watershed, and had an equal amount of upland and riparian plots. Out of the 42 total plots, 8 were situated in riparian areas and the rest were in the upland.

At each plot, gas wells have been installed at depths of 5, 20, and 50 cm. The specific design of each well was the same as that described in Pacific et al. (2011), with all wells being constructed from 2-inch diameter PVC pipe. The tops were sealed with a #11 rubber stopper (VWR International, Radnor, Pennsylvania), through which two 1m-long clear plastic PVC tubes were passed (ThermoFisher Scientific Nalgene, Waltham, Massachusetts). At the soil surface, the tubes were connected using quick connect couplers (Cole-Parmer, Vernon Hills, Illinois) and secured using cable ties. This design
was slightly modified for wells that were installed at 5cm. The bottoms of these wells were sealed with PVC plugs and two small windows centered at 5cm were cut out of the sides of the each well.

The soil CO$_2$ of each gas well was measured at weekly to subweekly time intervals, using a handheld carbon dioxide meter (Vaisala GM70, Finland). 180 mL of soil CO$_2$ was then extracted from each well and injected into a Tedlar sample bag (SKC Inc., Eighty Four, PA) that had been previously flushed with nitrogen. The volumetric water content of the soil at a range of 0-12 cm (HydroSense, Campbell Scientific, UT), soil temperature (12 cm soil thermometer, Reotemp Instrument Corporation, San Diego, CA), and soil CO$_2$ efflux (EGM-4 with SRC-1 respiration chamber, PP Systems, Amesbury, MA) were measured three times at each plot concurrently with soil CO$_2$ extraction. The bulk $\delta^{13}$C-CO$_2$ ($\delta_{\text{BULK}}$) of each sample was determined using a Cavity Ring-Down Spectroscopy (CRDS) analyzer (Picarro G-2101i, Picarro Inc., Sunnyvale, California).

Two standard gases were used to calibrate the performance of the CRDS analyzer. The first standard was a certified mixture of 1000 ppm CO$_2$ in air (Matheson/Linweld Inc., Lincoln NE). This standard was measured before and after daily analysis, as well as periodically between gas samples. These measurements were used to correct the bulk $\delta^{13}$C-CO$_2$ results reported by the CRDS analyzer for daily drift. The second air standard was an isotopic standard, which was calibrated by the Stable Isotope Lab (SIL) at the University of Colorado. This was measured in conjunction with the first standard for four
times throughout the field season. The results from these measurements were then used to correct bulk $\delta^{13}$C-CO$_2$ for seasonal variability.

All isotope values were reported using the delta notation ($\delta_p$), which measures the deviation of the ratio of $^{13}$C and $^{12}$C in a sample from the $^{13}$C and $^{12}$C ratio in the international standard of Vienna Pee Dee Belemnite (VPDB) (Craig 1957; Farquhar et al. 1989). The equation of the delta notation is the following:

$$\delta_p = \frac{R_p - R_s}{R_s} = \frac{R_p}{R_s} - 1$$

where $R_p = ^{13}$C/$^{12}$C of sample and $R_s = ^{13}$C/$^{12}$C of VPDB. Delta notations are reported in units of permille ($\‰$).

All $\delta^{13}$C-CO$_2$ measurements from the CRDS analyzer were corrected for instrument drift and seasonal variability as described in the previous section. Calibrated $\delta^{13}$C-CO$_2$ values that were equal or greater than the atmospheric value of -8‰ were not included in analysis.

**Isotopic Data Analysis**

From the calibrated bulk $\delta^{13}$C-CO$_2$ measurements ($\delta_{BULK}$), the $\delta^{13}$C-CO$_2$ of biological production was first estimated using the Keeling plot method (Keeling, 1958). It is a two-component linear mixing model where the isotopic ratio of atmospheric CO$_2$ varies linearly with 1/CO$_2$ and the isotope ratio of atmospheric CO$_2$ and the isotope ratio of the CO$_2$ source are the end members. $\delta^{13}$C-CO$_2$ of production ($\delta_{PROD}$) at each depth
was also estimated using the complementary model developed by Davidson (1995) and Bowling et al. (2008):

$$\delta_{PROD} = \frac{C_{BULK}(\delta_{BULK} - 4.4) - C_a(\delta_a - 4.4)}{1.0044(C_{BULK} - C_a)} \%$$

where $\delta_a$ is the isotopic ratio of atmospheric CO$_2$, which was assumed to be a constant -8 ‰, $C_a$ is the atmospheric CO$_2$ concentration, also assumed to be a constant 392 ppm, $\delta_{BULK}$ is the isotopic ratio of the soil gas as previously defined, and $C_{BULK}$ is the corresponding CO$_2$ concentration of soil gas. In contrast with the Keeling plot, where the isotopic ratio of soil CO$_2$ production is estimated using measurements at different depths, only two points are needed for the Davidson-derived equation: an atmospheric CO$_2$ measurement and a soil gas measurement. Davidson $\delta_{PROD}$ values were compared to Keeling $\delta_{PROD}$ values using one-way ANOVA. $\delta_{PROD}$ values calculated using the Davidson methodology were used in analysis as the $\delta_{PROD}$ at different depths can be estimated. After a value for $\delta_{PROD}$ was obtained, the change in soil $\delta^{13}$C-CO$_2$ that is associated with physical fractionation and mixing of air from the atmosphere ($\Delta_{DIFF}$) was then calculated by subtracting $\delta_{PROD}$ from $\delta_{BULK}$.

CO$_2$ concentrations reported throughout the study were absolute values measured by the CRDS analyzer in parts per million (ppm). Soil CO$_2$ efflux (g CO$_2$/ m$^2$/hr), soil temperature ($^\circ$C) and soil moisture (%) values used in all analyses were the average of three readings taken at each plot. Individual plots were classified as riparian or upland, depending on their location. Five transects (NWC, NWD, SW, WH, and SPC) were located in upland areas, and two transects (T1 and T2), had plots spanning both upland
and riparian areas. Out of 42 total plots, 34 are classified as upland and 8 are riparian. This discrepancy between the number of upland and riparian plots parallels the composition of the watershed, where riparian areas are less than 2% of the total landscape (Riveros-Iregui, 2008).

After plot classification, seasonal soil moisture variability was examined by calculating the weekly average of all soil moisture readings, along with the associated standard error. $\delta_{\text{PROD}}, \delta_{\text{BULK}}, \Delta_{\text{DIFF}},$ and soil CO$_2$ concentration values were separated by depth and averaged weekly for comparison with average seasonal upland/riparian soil moisture variability. Soil CO$_2$ efflux was also averaged weekly, again for comparison to seasonal soil moisture variability. The standard error of all averages was calculated. The separate average weekly soil moisture, $\delta_{\text{PROD}}, \delta_{\text{BULK}}, \Delta_{\text{DIFF}},$ soil CO$_2$ concentration, and soil CO$_2$ efflux of riparian and upland areas were also calculated.

Soil moisture was binned based on early, middle, and late seasons, roughly 1-3, 4-6, and 7-9 weeks. Data collected ($\delta_{\text{PROD}}, \delta_{\text{BULK}}, \Delta_{\text{DIFF}},$ soil CO$_2$ concentration, and soil CO$_2$ efflux) was binned into three groups based on the time of the growing season. Specific riparian/upland trios of weeks were compared to their counterpart (ex. Weeks 1-3 Riparian vs. Weeks 1-3 Upland) as well as to other trios of weeks in the same landscape category (ex. Weeks 1-3 Riparian vs. Weeks 4-6 Riparian vs. Weeks 7-9 Riparian). The Lilliefors test (Lilliefors, 1967) and visual inspection of quartile-quartile plots were used to determine the normality of data groups. The equality of group variances was then examined using Bartlett’s test (Bartlett, 1937) As the majority of groups tested had non-
normal distributions and unequal variances, Welch’s one-way ANOVA (Welch, 1951) was used for group comparison. If a significant difference between test groups was identified, the Games-Howell (Games & Howell, 1976) post-hoc test was performed.

Ordinary least squares regressions were performed with $\delta_{\text{PROD}}, \delta_{\text{BULK}}, \text{soilCO}_2$ concentration, and soil CO$_2$ efflux as the dependent variables and soil moisture and soil temperature as independent variables. Two sets of regressions were calculated: the first with either soil moisture or soil temperature as the sole independent variable and the second with both soil moisture and soil temperature as independent variables. These two sets of regressions were executed at different scales: using all sites, by plot classification (upland or riparian), by transect, and by individual plot. An additional set of regressions was performed with $\delta_{\text{PROD}}$ and $\delta_{\text{BULK}}$ as dependent variables and soil moisture and soil CO$_2$ efflux as the independent variables. These were also calculated at the same scales as the previous sets of regressions.

**Statistical Analysis**

The value of the upslope accumulated area (UAA, measured in units of m$^2$) of all plots included in the study watershed were calculated by K. Kaiser (personal communication, 2014). This topographic metric measures the total area that drains to a selected point in a watershed and has been used to represent the lateral redistribution of water in a landscape (Jencso et al., 2009). Riveros-Iregui & McGlynn (2009) demonstrated that UAA is a predictor of soil CO$_2$ efflux at the landscape level and successfully developed a watershed-scale soil CO$_2$ efflux model based on UAA. The
UAA at each individual plot had been previously calculated using a digital elevation model (DEM) with a resolution of 6m according to the method developed by Seibert & McGlynn (2007). Four of the riparian sites were in very close proximity to stream cells in the DEM and therefore had problematic values (K. Kaiser, personal communication, 2014). These sites were not included in UAA analysis. Topographic Wetness Index (TWI) values calculated from the same DEM were also used in the study. UAA and TWI were compared to soil CO₂ flux, as well as δᵣₒₚᵢᵣₒᵣ, δᵦᵣᵦₐᵦᵦ, Δᵦᵦᵦᵦ, and soilCO₂ concentration grouped by depth, using ordinary least squares regression.

SPSS 19 (IBM, Armonk, NY) was used to execute both Welch’s ANOVA and the Games-Howell post-hoc test. All other data and statistical analyses were performed using MATLAB 2012b (The MathWorks Inc. Natick, MA).

RESULTS

Soil Moisture Across the Field Site
Figure 2.1 Weekly average soil moisture of upland and riparian areas

The average soil moisture values of upland and riparian areas exhibited different patterns throughout the growing season (Figure 2.1). From an average of 25% in the first three weeks, soil moisture in upland areas decreased sharply in weeks 4-6 until it reached the single digits in the last three weeks of measurements. In contrast, the soil moisture values in riparian sites remained consistently high throughout the growing season and decreased gradually, only dipping below 30% in the last three weeks of sampling. While a sharp soil moisture drydown was observed in upland areas, riparian areas retained a high amount of moisture throughout the growing season, and only exhibited a minor drydown towards the end of the sampling period.
Temporal CO₂ Patterns in Upland and Riparian Areas

Figure 2.2 shows δ¹³C-CO₂, CO₂ flux, and CO₂ concentration data averaged by week, with the error bars again representing the standard error of the mean. Values of average δBULK at all depths increased slightly from the start of measurement before decreasing in the last 2 weeks of measurement. The calculated δPROD values followed the same pattern, with increased variability observed in the last three weeks of measurement. δBULK values also decreased with depth. This inverse relationship of soil δBULK with depth has been attributed to increased mixing with enriched atmospheric δ¹³C-CO₂ (~8‰) at shallow depths and fractionation from plant processes, primarily photosynthesis. (Bowling et al., 2008; Hesterberg & Siegenthaler, 1991). Soil CO₂ concentration
increased with depth, and all depths followed the same temporal pattern. After a small increase in the first few weeks, CO₂ concentrations decreased from the fourth to sixth weeks then stabilized during the last 3 weeks, corresponding to the soil moisture pattern of upland areas in Figure 2.1. The magnitude of decrease was greatest in soil CO₂ concentrations at 50 cm. CO₂ flux values in upland areas were lower than .4 g CO₂ m⁻² hr⁻¹, save for a spike in late June. The variability of average ΔDIFF was highest at 5 cm. As soil moisture was at its peak in the first three weeks, average upland ΔDIFF decreased to a minimum, and then increased slowly throughout the field season, corresponding to the seasonal drydown in upland sites. The mid-July spike in 5 cm ΔDIFF was due to an outlier.

![Graphs of δ¹³C-CO₂, CO₂ flux, and CO₂ concentration of riparian areas.](image)

**Figure 2.3** Average weekly δ¹³C-CO₂, CO₂ flux, and CO₂ concentration of riparian areas.

The temporal patterns of δ¹³C-CO₂, CO₂ flux, and soil CO₂ concentration in riparian sites differed from those in the upland sites. In contrast with upland areas, there
was no clear trend in the average $\delta_{\text{BULK}}$ of riparian areas. $\delta_{\text{BULK}}$ values also overlapped at different depths (Figure 2.3), as opposed to the upland sites where the average $\delta_{\text{BULK}}$ of each depth was distinct from the others. The weekly average $\delta_{\text{PROD}}$ was also very variable. The value of weekly average $\Delta_{\text{DIFF}}$ was only slightly lower in riparian areas compared to upland $\Delta_{\text{DIFF}}$. Similar to the pattern of upland $\Delta_{\text{DIFF}}$, average riparian $\Delta_{\text{DIFF}}$ at all depths started high then decreased until the first of July, after which it increased, most notably at 5 cm compared to 20 and 50 cm. As with riparian $\delta^{13}\text{C-CO}_2$, riparian soil CO$_2$ concentrations were very variable. At 50 cm, CO$_2$ concentrations increased until the first week of July and then fluctuated before stabilizing and ending at the highest CO$_2$ concentration of the season. Although very variable, 20 cm CO$_2$ concentration also trended upwards, while 5 cm CO$_2$ concentration remained steady at a low value throughout the period of study, except for a spike in the second week. The upward trend of CO$_2$ concentrations at 20 cm and 50 cm indicate greater production at as sites dry out from their initial saturation due to snowmelt (Pacific et al., 2008). In contrast to the CO$_2$ flux at upland sites, two peaks were observed in the flux at riparian sites- the first at the start of July and the second at its end. Riparian CO$_2$ flux was also higher than upland CO$_2$ flux.
Figure 2.4. Comparison of δ\(^{13}\)C-CO\(_2\) variables between upland and riparian areas using Welch’s ANOVA. Stars (*) indicate significant difference between groups (p < 0.05).

The variability of δ\(_{\text{BULK}}\), δ\(_{\text{PROD}}\), and Δ\(_{\text{DIFF}}\) was higher in upland areas than in riparian areas, specifically during weeks 1-3 (Figure 2.4). Although a majority of upland δ\(_{\text{BULK}}\) values were within the range of soil δ\(^{13}\)C-CO\(_2\) and δ\(^{13}\)C-CO\(_2\) of soil and C\(_3\) ecosystem respiration previously observed in the literature (Davidson, 1995; Bowling et
al. 2007) there were many outliers that were either more negative than this range or near the atmospheric value $\delta^{13}$C-CO$_2$ of -8. The calculated $\delta_{\text{PROD}}$ values were even more negative than $\delta_{\text{BULK}}$, especially in riparian areas during weeks 1-6. Although the median of upland $\delta_{\text{BULK}}$ was higher than that of riparian $\delta_{\text{BULK}}$ during weeks 4-9 of the sampling period, the only significant difference between the two was in weeks 4-6 (Figure 2.6). This difference was not observed in either $\delta_{\text{PROD}}$ or $\Delta_{\text{DIFF}}$ in weeks 4-6, though the median upland $\delta_{\text{PROD}}$ and $\Delta_{\text{DIFF}}$ were both higher than riparian $\delta_{\text{PROD}}$ and $\Delta_{\text{DIFF}}$ at that time. There was no significant difference between the calculated $\delta_{\text{PROD}}$ of upland and riparian areas at any time. Although the average of upland $\Delta_{\text{DIFF}}$ readings was higher than riparian $\Delta_{\text{DIFF}}$ at all times, the only significant difference between the two was in weeks 7-9, which did not correspond with the trend of $\delta_{\text{BULK}}$. 
Binned \( \delta_{\text{BULK}} \), \( \delta_{\text{PROD}} \), and \( \Delta_{\text{DIFF}} \) were compared within riparian and upland sites. There were no significant differences within riparian \( \delta_{\text{BULK}} \), \( \delta_{\text{PROD}} \), or \( \Delta_{\text{DIFF}} \) at all times. In contrast, upland \( \delta_{\text{BULK}} \) in weeks 4-6 and 7-9 were both significantly higher than \( \delta_{\text{BULK}} \) in weeks 1-3 and were not significantly different from each other. Upland \( \delta_{\text{PROD}} \) followed the same trend as \( \delta_{\text{BULK}} \). Although the median and range of upland \( \Delta_{\text{DIFF}} \) values increased throughout the growing season, there was no significant difference between binned \( \Delta_{\text{DIFF}} \) at any time.
Figure 2.6. Comparison of CO₂ concentration and flux between and within upland and riparian sites using Welch’s ANOVA. Stars (*) indicate significant difference between groups (p <0.05).

At the start of the sampling season, there was no significant difference between the CO₂ concentration of upland or riparian areas (Figures 2), but the values diverged as the growing season progressed. By the end of the growing season, upland CO₂ concentration had decreased significantly, while CO₂ concentration in riparian areas increased, but not significantly. Although riparian CO₂ flux was significantly higher than that of upland areas during all weeks, they shared the same parabolic pattern, which previously attributed to be due the stimulation by soil moisture of heterotrophic and autotrophic soil CO₂ production (Kowalenko, 1978 et. al; Davidson et al., 2000). Models have shown that soil moisture generally enhances both soil CO₂ concentration and CO₂
flux, although at very high soil moisture levels both gas diffusivity and production can be inhibited (Davidson et al., 2000; Hashimoto & Komatsu, 2006).

Table 2.1. Correlation coefficient of binned soil moisture with topographic attributes

<table>
<thead>
<tr>
<th>Week</th>
<th>UAA</th>
<th>TWI</th>
<th>Elevation</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Weeks</td>
<td>.06</td>
<td>.02</td>
<td>-.33**</td>
</tr>
<tr>
<td>Weeks 1-3</td>
<td>.10</td>
<td>.04</td>
<td>-.38**</td>
</tr>
<tr>
<td>Weeks 4-6</td>
<td>.08</td>
<td>.02</td>
<td>-.46**</td>
</tr>
<tr>
<td>Weeks 7-9</td>
<td>.04</td>
<td>.06</td>
<td>-.36**</td>
</tr>
</tbody>
</table>

* significant, p <.05
** highly significant, p<.0001

I compared field-measured soil moisture with three topographical attributes that had been previously calculated from a 6m digital elevation model (DEM): upslope accumulated area (UAA), topographic wetness index (TWI), and elevation. The TWI and UAA values of half the riparian sites were unreliable as they were located in the stream cells of the DEM (K. Kaiser, personal communication), and so were excluded from correlation and regression analysis. Out of the three topographic attributes considered, elevation was the sole attribute that was significantly correlated with soil moisture (Table 2.1). The correlation between the two was highest during the middle of the sampling period, corresponding with the seasonal drydown, and lowest during three weeks of sampling, when the landscape was at its driest.
The correlation between topographical attributes and soil moisture was repeated using data of riparian and upland areas of the landscape (Table 2.2). Only one significant correlation was found in riparian sites for all topographical attributes and times considered. This was expected, as there is no significant topographical variation in the riparian sites. As riparian areas compose only 2% of the total catchment area (Pacific et al., 2008), the significant inverse correlation between elevation and soil moisture observed in the total catchment area held true for upland sites. Again, the correlation between soil moisture and elevation was highest during the soil moisture drydown and lowest during the period when the landscape was the driest.

### Table 2.2. Correlation coefficient of binned soil moisture with topographical attributes in riparian and upland areas.

<table>
<thead>
<tr>
<th>Time</th>
<th>Riparian</th>
<th>Upland</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UAA</td>
<td>TWI</td>
</tr>
<tr>
<td>All Weeks</td>
<td>.17</td>
<td>.05</td>
</tr>
<tr>
<td>Weeks 1-3</td>
<td>.05</td>
<td>.20</td>
</tr>
<tr>
<td>Weeks 4-6</td>
<td>.01</td>
<td>-.30</td>
</tr>
<tr>
<td>Weeks 7-9</td>
<td>.65*</td>
<td>.28</td>
</tr>
</tbody>
</table>

* significant, p <.05  
**highly significant, p<.0001

### Table 2.3 Correlation coefficient (r) of δ¹³C-CO₂, soil CO₂, soil moisture, and topographic attributes in riparian and upland areas.

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Riparian</th>
<th>Upland</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>δ_BULK</td>
<td>δ_PROD</td>
</tr>
<tr>
<td>Soil Moisture</td>
<td>-.17</td>
<td>-.11</td>
</tr>
<tr>
<td>Elevation</td>
<td>.18</td>
<td>.09</td>
</tr>
<tr>
<td>TWI</td>
<td>.01</td>
<td>.08</td>
</tr>
<tr>
<td>UAA</td>
<td>.02</td>
<td>.09</td>
</tr>
</tbody>
</table>

* significant, p <.05  
**highly significant, p<.0001
Table 2.3 shows the correlation of $\delta_{\text{BULK}}, \delta_{\text{PROD}}, \Delta_{\text{DIFF}}$, with soil moisture and calculated topographic attributes in riparian and upland areas. In upland areas, soil moisture and elevation were significantly correlated with almost all variables considered. Upland CO$_2$ concentration and CO$_2$ flux were positively correlated with soil moisture and inversely correlated with elevation. Both upland $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ were significantly correlated with elevation, and $\delta_{\text{BULK}}$ was negatively correlated with soil moisture. The CO$_2$ concentration and CO$_2$ flux of riparian sites were positively correlated with soil moisture, but were not significantly correlated with elevation. Both riparian $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ were not significantly correlated with soil moisture or any of the topographic attributes. Although there was no significant correlation between riparian $\Delta_{\text{DIFF}}$ and soil moisture, riparian $\Delta_{\text{DIFF}}$ was significantly correlated with all topographic attributes. It was positively correlated with elevation and inversely correlated with both TWI and UAA.

Table 2.4 Correlation coefficient ($r$) of binned $^{13}$C-CO$_2$ and soil CO$_2$ with soil moisture and topographic attributes in riparian and upland areas.

<table>
<thead>
<tr>
<th>Attribute and Time</th>
<th>Riparian</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{\text{BULK}}$</td>
<td>$\delta_{\text{PROD}}$</td>
<td>$\Delta_{\text{DIFF}}$</td>
<td>CO$_2$</td>
<td>CO$_2$ Flux</td>
<td>$\delta_{\text{BULK}}$</td>
<td>$\delta_{\text{PROD}}$</td>
<td>$\Delta_{\text{DIFF}}$</td>
<td>CO$_2$</td>
<td>CO$_2$ Flux</td>
</tr>
<tr>
<td>Soil Moisture (Wks 1-3)</td>
<td>-.12</td>
<td>-.37</td>
<td>.06</td>
<td>.16</td>
<td>.09</td>
<td>-.25**</td>
<td>-.05</td>
<td>.02</td>
<td>.25**</td>
<td>.10</td>
</tr>
<tr>
<td>Soil Moisture (Wks 4-6)</td>
<td>-.26</td>
<td>-.16</td>
<td>.31</td>
<td>.31</td>
<td>.38</td>
<td>-.21*</td>
<td>-.10</td>
<td>.12*</td>
<td>.27*</td>
<td>.61**</td>
</tr>
<tr>
<td>Soil Moisture (Wks 7-9)</td>
<td>-.17</td>
<td>.12</td>
<td>.24</td>
<td>.37</td>
<td>.63**</td>
<td>.001</td>
<td>-.03</td>
<td>.03</td>
<td>.26**</td>
<td>.42**</td>
</tr>
<tr>
<td>Elevation (Wks 1-3)</td>
<td>.16</td>
<td>.42</td>
<td>.09</td>
<td>-.34</td>
<td>.78**</td>
<td>.27**</td>
<td>.16*</td>
<td>.08</td>
<td>-.17*</td>
<td>-.14</td>
</tr>
<tr>
<td>Elevation (Wks 4-6)</td>
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<td>.76</td>
<td>.28</td>
<td>-.25</td>
<td>.04</td>
<td>.28**</td>
<td>.13*</td>
<td>.07</td>
<td>-.19*</td>
<td>-.23*</td>
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<td>--------</td>
</tr>
<tr>
<td>Elevation (Wks 7-9)</td>
<td>.07</td>
<td>.07</td>
<td>.41*</td>
<td>.07</td>
<td>.16</td>
<td>.08</td>
<td>.06</td>
<td>.02</td>
<td>-.11</td>
<td>-.11</td>
</tr>
<tr>
<td>TWI (Wks 1-3)</td>
<td>.13</td>
<td>.25</td>
<td>.00</td>
<td>.11</td>
<td>.12</td>
<td>.03</td>
<td>.07</td>
<td>.03</td>
<td>.09</td>
<td>.01</td>
</tr>
<tr>
<td>TWI (Wks 4-6)</td>
<td>.34</td>
<td>.45*</td>
<td>.20</td>
<td>.03</td>
<td>-.36*</td>
<td>.04</td>
<td>.03</td>
<td>.04</td>
<td>.04</td>
<td>.05</td>
</tr>
<tr>
<td>TWI (Wks 7-9)</td>
<td>-.15</td>
<td>.00</td>
<td>-.20</td>
<td>.20</td>
<td>.69**</td>
<td>.04</td>
<td>-.14*</td>
<td>.08</td>
<td>.04</td>
<td>.02</td>
</tr>
<tr>
<td>UAA (Wks 1-3)</td>
<td>.06</td>
<td>.13</td>
<td>.23</td>
<td>.01</td>
<td>.09</td>
<td>.06</td>
<td>.003</td>
<td>.10</td>
<td>.01</td>
<td>.07</td>
</tr>
<tr>
<td>UAA (Wks 4-6)</td>
<td>.26</td>
<td>.32</td>
<td>.23</td>
<td>.24</td>
<td>.35</td>
<td>.002</td>
<td>.04</td>
<td>.02</td>
<td>.02</td>
<td>.06</td>
</tr>
<tr>
<td>UAA (Wks 7-9)</td>
<td>-.31</td>
<td>.20</td>
<td>-.65*</td>
<td>.42*</td>
<td>.63**</td>
<td>-.06</td>
<td>-.11</td>
<td>.01</td>
<td>.05</td>
<td>.13*</td>
</tr>
</tbody>
</table>

* significant, p < .05  
**highly significant, p < .0001

Elevation was significantly correlated with both upland $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ during the first six weeks of sampling (Table 2.4), spanning the period when the landscape is at its wettest, until it dries out. $\delta_{\text{BULK}}$ was also inversely correlated with soil moisture during the same period of time. Upland CO$_2$ concentration and flux, on the other hand, was significantly correlated with both soil moisture and elevation during all weeks. There were no patterns associated with upland $\delta^{13}$C-CO$_2$ or CO$_2$ flux variables and TWI and UAA, as there were only two isolated significant correlations. In riparian areas, CO$_2$ flux was significantly positively correlated with elevation during weeks 1-3 and with soil moisture and UAA during the latter part of the sampling period, from weeks 4-9. Although TWI was also significantly correlated with CO$_2$ flux during weeks 4-9, the correlations conflicted with each other. UAA during weeks 7-9 was also positively correlated with CO$_2$ concentration and inversely correlated with $\Delta_{\text{DIFF}}$. During the same period of time, $\Delta_{\text{DIFF}}$ was also positively correlated with elevation. The significant
correlation of all riparian ΔDIFF values with TWI previously observed did not manifest when ΔDIFF values were separated by time and then correlated with TWI.

Table 2.5. Coefficient of individual predictors and coefficient of determination of multiple regression models predicting CO₂ flux.

<table>
<thead>
<tr>
<th>Week</th>
<th>Attribute Coefficient</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UAA</td>
<td>TWI</td>
</tr>
<tr>
<td>All Weeks</td>
<td>.000015</td>
<td>-.02</td>
</tr>
<tr>
<td>Weeks 1-3</td>
<td>.000034</td>
<td>-.043</td>
</tr>
<tr>
<td>Weeks 4-6</td>
<td>.0000015</td>
<td>-.013</td>
</tr>
<tr>
<td>Weeks 7-9</td>
<td>.000024</td>
<td>-.019</td>
</tr>
</tbody>
</table>

*Bolded* values indicate p values <.05

UAA, TWI, elevation, soil moisture, and carbon dioxide concentration were incorporated into a multiple regression model as possible predictors of CO₂ flux. The power of this model and the significance of each predictor were examined, both overall and separated into the same sets of weeks used in previous correlations. The model performed best during weeks 4-6 and weeks 7-9, explaining 35% and 33% of the variation of CO₂ flux, respectively. Soil moisture was the sole significant predictor of CO₂ flux in weeks 4-6, while both soil moisture and UAA were significant predictors in weeks 7-9, consistent with correlation results. The same model explained less than 10% of CO₂ flux variation overall and during weeks 1-3.

Table 2.6 Coefficient of individual predictors and coefficient of determination of multiple regression models predicting CO₂ concentration at different depths.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Time</th>
<th>Attribute Coefficient</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UAA</td>
<td>TWI</td>
<td>Elevation</td>
</tr>
<tr>
<td>All</td>
<td>All Weeks</td>
<td>-.06</td>
<td>202.90</td>
</tr>
<tr>
<td></td>
<td>Weeks 1-3</td>
<td>-.22</td>
<td>504.051</td>
</tr>
<tr>
<td></td>
<td>Weeks 4-6</td>
<td>-.082</td>
<td>205.018</td>
</tr>
<tr>
<td></td>
<td>Weeks 7-9</td>
<td>.117</td>
<td>-137.20</td>
</tr>
<tr>
<td>5 cm</td>
<td>All Weeks</td>
<td>-.004</td>
<td>-15.246</td>
</tr>
</tbody>
</table>
A multiple regression model with soil moisture and the three topographic attributes as inputs predicting CO\textsubscript{2} concentration at all depths and at specific depths was most successful at predicting 5cm and 20 cm CO\textsubscript{2} concentration (Table 2.6). Only 10% of the variation of CO\textsubscript{2} concentration at all depths was predicted, improving to 18%, 20%, and 16% for 5 cm, 20 cm, and 50 cm respectively. The variance of CO\textsubscript{2} concentration at all depths accounted for by the model improved as the field season progressed, and this was also true for CO\textsubscript{2} concentrations at 20 cm. For 5cm CO\textsubscript{2} concentrations, however, the model was most successful during the first six weeks of measurement. Soil moisture and elevation were significant predictors of CO\textsubscript{2} concentrations at all times for all depths, 20cm, and 50cm. Soil moisture was the sole significant predictor of 5cm CO\textsubscript{2} at all times examined, as well as of 20 cm during weeks 4-9. Topographic attributes were significant predictors of CO\textsubscript{2} concentration at all depths, 20 cm, and 50 cm only during the wettest time of the season.
Table 2.7. Coefficient of individual predictors and coefficient of determination of multiple regression models predicting $\delta_{BULK}$ at different depths.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Time</th>
<th>Attribute</th>
<th>Coefficient</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>UAA</td>
<td>TWI</td>
</tr>
<tr>
<td>All</td>
<td>All Weeks</td>
<td></td>
<td>.00</td>
<td>-.26</td>
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<td></td>
<td>Weeks 1-3</td>
<td></td>
<td>.00</td>
<td>-.56</td>
</tr>
<tr>
<td></td>
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<td>-.34</td>
</tr>
<tr>
<td></td>
<td>Weeks 7-9</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 cm</td>
<td>All Weeks</td>
<td></td>
<td>.00</td>
<td>-.13</td>
</tr>
<tr>
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<td></td>
<td>Weeks 4-6</td>
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<td>.000099</td>
<td>.228</td>
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<tr>
<td></td>
<td>Weeks 7-9</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20 cm</td>
<td>All Weeks</td>
<td></td>
<td>.00</td>
<td>-.38</td>
</tr>
<tr>
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<td>-.56</td>
</tr>
<tr>
<td></td>
<td>Weeks 7-9</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50 cm</td>
<td>All Weeks</td>
<td></td>
<td>.000042</td>
<td>-.21</td>
</tr>
<tr>
<td></td>
<td>Weeks 1-3</td>
<td></td>
<td>.00</td>
<td>-.27</td>
</tr>
<tr>
<td></td>
<td>Weeks 4-6</td>
<td></td>
<td>.00</td>
<td>-.705</td>
</tr>
<tr>
<td></td>
<td>Weeks 7-9</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Bolded** values indicate p values < 0.05

- indicates that the multiple regression model or specific attribute was not statistically significant.

Soil moisture and elevation were the main significant predictors of $\delta_{BULK}$ (Table 2.7). A model predicting $\delta_{BULK}$ values at all depths and all times explained 10% of the variation. This improved slightly to 15% and 14% when only 5cm and 20cm $\delta_{BULK}$ throughout the whole season were considered, respectively. As with CO$_2$ concentration, the variation of $\delta_{BULK}$ at all depths and at 20 cm explained by the model increased from weeks 1-3 to weeks 4-6. Soil moisture, elevation, and flux were significant predictors of $\delta_{BULK}$ at all depths as well as at 50 cm for all weeks of the field season, while only soil moisture and elevation were significant predictors of 5cm and 20 cm $\delta_{BULK}$ for the same time period. None of the multiple regression models were significant at weeks 7-9.
Table 2.8. P-value of individual predictors and coefficient of determination of multiple regression models predicting $\delta_{\text{PROD}}$ calculated using data from different depths.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Time</th>
<th>Attribute</th>
<th>Coefficient</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>UAA</td>
<td>TWI</td>
<td>Elevation</td>
</tr>
<tr>
<td>All</td>
<td>All Weeks</td>
<td>.00</td>
<td>.25</td>
<td>.005</td>
</tr>
<tr>
<td></td>
<td>Weeks 1-3</td>
<td>.00</td>
<td>.84</td>
<td>.004</td>
</tr>
<tr>
<td></td>
<td>Weeks 4-6</td>
<td>.00</td>
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<td>.009</td>
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<tr>
<td>5 cm</td>
<td>All Weeks</td>
<td>-</td>
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<td>-</td>
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<td>Weeks 1-3</td>
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<td>Weeks 4-6</td>
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<td>.91</td>
<td>.02</td>
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<td>Weeks 7-9</td>
<td>-</td>
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<tr>
<td>20 cm</td>
<td>All Weeks</td>
<td>-</td>
<td>-</td>
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</table>

Bolded values indicate p values < .05 - indicates that the multiple regression model or specific attribute was not statistically significant.

Multiple regression models with the same attributes used to predict $\delta_{\text{BULK}}$ were not successful in predicting the majority of $\delta_{\text{PROD}}$ values (Table 2.8). Elevation and UAA were the main significant predictors of all $\delta_{\text{PROD}}$ values, and from weeks 1-6, but the model only explained a maximum of 6% of $\delta_{\text{PROD}}$ variation. The model chosen only accounted for 17% of the variation of 5cm $\delta_{\text{PROD}}$ and 11% of the variation 20cm $\delta_{\text{PROD}}$ during weeks 4-6. It was also not significant in predicting the variation of 50 cm $\delta_{\text{PROD}}$ at any point in the field season.
Table 2.9. P-value of individual predictors and coefficient of determination of multiple regression models predicting $\Delta_{DIFF}$ at different depths.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Time</th>
<th>Attribute</th>
<th>UAA</th>
<th>TWI</th>
<th>Elevation</th>
<th>VWC</th>
<th>Flux</th>
<th>$R^2$</th>
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</thead>
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<td>Weeks 7-9</td>
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</tr>
<tr>
<td>20 cm</td>
<td>All Weeks</td>
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<td>-.339</td>
<td>.006</td>
<td>-.001</td>
<td>-1.07</td>
<td>.036</td>
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<td>Weeks 1-3</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Weeks 4-6</td>
<td>.00</td>
<td>-.70</td>
<td>.011</td>
<td>-.05</td>
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**Bolded** values indicate p values <.05
- indicates that the multiple regression model or specific attribute was not statistically significant.

The same model used to predict $\delta_{PROD}$ and $\delta_{BULK}$ was not significant for the majority of $\Delta_{DIFF}$ values (Table 2.9). The model was only significant during weeks 7-9 for 20 cm $\Delta_{DIFF}$ and all weeks of 50 cm $\Delta_{DIFF}$, with only soil moisture and elevation as the significant predictors. Only 13% and 5% of the variation in $\Delta_{DIFF}$ for the two groups of weeks was explained by the model.

**DISCUSSION**

**Spatial Variation of Soil Moisture and Correlation with Topographic Attributes**

Soil moisture values in well-drained upland areas were significantly lower than soil moisture in riparian areas (one-way ANOVA, p <.01). This can be attributed to the topographical location of sites relative to streams and the shallow, coarser texture of the soil in upland sites compared to the poorly-drained soil found in riparian sites. Due to
their difference in surface soil moisture, riparian and upland areas can be considered as separate hydrologic units (Henninger et al., 1976). Whereas riparian soil moisture remained at a high level throughout the field season, three distinct soil moisture trends were observed in upland areas: 1) a wet period spanning the first three weeks, 2) drydown spanning weeks 4-6, and 3) dry period during weeks 7-9 (Figure 1).

![Figure 2.7 Plot-level Soil Moisture Variance. Soil moisture readings in individual plots were binned in groups of three weeks according to the distinct soil moisture trends observed. The mean and the standard deviation of the binned readings per plot were then calculated. These three trends were also observed at the plot level (Figure 2.7). The distinct clusters of upland plots show the clear transition, while the soil moisture of riparian plots remained high, even at the end of the field season. Soil moisture variability in plots followed a convex shape, with the highest variability of both riparian and upland areas occurring at intermediate soil moisture values, in agreement with previous studies that have used a higher number of measurements. When the catchment is at its wettest, soil]
moisture variability is controlled by soil porosity and hydraulic conductivity (Vereecken et al., 2007). As the catchment dries out, soil moisture variability increases due to the spatial heterogeneity of these properties, and then decreases as soil moisture levels become more uniform across the landscape and the importance of evapotranspiration as a control of soil moisture increases (Korres et al., 2015; Pan & Peters - Lidard, 2008).

Both soil moisture throughout the landscape and soil moisture in upland areas were strongly inversely correlated with elevation, which integrates different topographic characteristics such as porosity, hydraulic conductivity, aspect, clay content, specific contributing area, wetness index, curvature, and soil depth (Famiglietti et al., 1998; Williams et al., 2009). This strong relationship was also observed in previous studies at different levels: separate plots in field sites with a minor elevation gradient, hillslope transect, and a small catchment (Brocca et al., 2007; Famiglietti et al., 1998; Krumbach, 1959; Williams et al., 2009; Yoo & Kim, 2004). For this study, the coefficient of determination of all soil moisture with elevation, though significant (p < .01), was only .096, lower than values recorded in the literature. The coefficient of determination of univariate topographic attributes with soil moisture in previous studies has rarely been greater than .50 (Famiglietti et al., 1998; Takagi & Lin, 2012; Western et al., 1999).

In contrast with elevation, neither UAA nor TWI was significantly correlated overall with soil moisture, even when upland and riparian areas were considered separately. This contradicts previous research which has successfully used TWI and the natural logarithm of UAA to predict watershed-scale soil moisture (Brocca et al., 2007; Nyberg, 1996; Tague et al., 2010; Western et al., 1999). A greater number of soil
moisture samples per plot may be needed to successfully establish watershed-scale relationships between TWI and UAA and soil moisture, as Tague et al. (2010) found that when surface soil moisture is measured weekly, a sample size of less than 5 soil readings per plot obscures the relationship between topographic position (indicated by TWI) and soil moisture. Another factor is the different scales between the data used to generate TWI and UAA and the point measurements of soil moisture in the field. Sources of soil moisture variability at scales smaller than 10m include the redistribution of water by tree roots (Brooks et al., 2002), heterogeneity in soil characteristics, disturbance by animals, and vegetation variation, while the contrast between hillslopes, including aspect, affects the variability at slightly larger scales (Coleman & Niemann, 2013). An important factor affecting soil moisture variability that was not considered in the study is evapotranspiration, which has been found to be a strong predictor of catchment-level soil moisture patterns, especially during dry periods (Coleman & Niemann, 2013; Takagi & Lin, 2012; Western et al., 1999) and related variables such as aspect and solar radiation (Buchanan et al., 2013). Buchanan et al., (2013) added soil transmissivity calculations to the standard TWI equation to account for soil drainage differences improves the prediction of watershed-scale soil moisture, and evapotranspiration has been combined with elevation to successfully predict the majority of watershed-scale soil moisture variation (Riley & Shen, 2014).
Spatial Variation of Soil $\delta^{13}$C-CO$_2$

Figure 2.0-8 Plot-Level Soil $\delta^{13}$C-CO$_2$ Variation. $\delta_{\text{BULK}}, \delta_{\text{PROD}},$ and $\Delta_{\text{DIFF}}$ per plot were binned as described in the previous figure.

In upland areas, $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ were significantly higher during the soil moisture drydown than at the start of the season, while maximum upland $\Delta_{\text{DIFF}}$ also increased throughout the growing season (Figure 2.5). In contrast, riparian $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ remained constant during the sampling period. The high variability of $\delta^{13}$C-CO$_2$ in upland sites during weeks 1-6 (Figures 2.4 and 2.8) may be due to the high variability of upland soil moisture during this time (Figure 2.7). The link between soil moisture and $\delta^{13}$C-CO$_2$, especially in upland areas, is supported by the significant inverse correlation of upland $\delta_{\text{BULK}}$ with soil moisture (Table 2.3) and the negative weight of soil moisture as a significant predictor of all $\delta_{\text{BULK}}$ values, as well as $\delta_{\text{BULK}}$ at 5 cm, 20 cm, and 50 cm (Table 2.7). These correlations followed the theoretical model proposed by Farquhar et al. (1989), where photosynthetic discrimination by C$_3$ plants is influenced by stomatal
conductance, which is in turn influenced by soil moisture limitation. Low soil moisture is expected to correspond to high $\delta^{13}$C-CO$_2$ in C$_3$ plants. This would be reflected in the $\delta^{13}$C-CO$_2$ of root respiration, and so in the $\delta^{13}$C-CO$_2$ of soil and soil respiration. Previous studies have also found that the temporal variation of the $\delta^{13}$C-CO$_2$ of soil and overall ecosystem respiration correspond to the response of autotrophic $\delta^{13}$C-CO$_2$ to soil moisture limitation consistent with the Farquhar model (Alstad et al., 2007; Ehleringer et al., 2002; Fessenden & Ehleringer, 2003; Risk et al., 2012). More negative $\delta_{\text{BULK}}$ has also been attributed to increased root respiration, with minimum $\delta_{\text{BULK}}$ occurring in conjunction with maximum soil CO$_2$ concentration and production (Hesterberg and Siegenthaler, 1991). In this study, this was only observed in the upland sites, where $\delta_{\text{BULK}}$ and CO$_2$ concentration were at their minimum and maximum, respectively, during the first 3 weeks of the field season (Figures 2.5 and 2.6). Following the Farquhar et al. (1989) model, $\delta_{\text{PROD}}$ is also expected to have a negative relationship with soil moisture, which has been observed in the field by Goffin et al. (2014) using the flux gradient method. In this study, $\delta_{\text{PROD}}$ calculated using the equation developed by Davidson (1995) was not significantly directly correlated with soil moisture.

The positive correlation of upland $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ with elevation (Table 2.3), and the positive weight of elevation as a significant predictor of all values of landscape-scale $\delta_{\text{BULK}}$, as well as landscape-scale $\delta_{\text{BULK}}$ at 5, 20, and 50 cm (Table 2.7) is consistent with previous research where carbon isotope discrimination in C$_3$ leaves decreases with altitude and both leaf and soil $\delta^{13}$C were observed to increase accordingly (Körner, 1991; Bird et al., 1994; Gieger and Leuschner, 2004; Hultine and Marshall, 1999). The needles
of *Pinus contorta* (lodgepole pine) in particular, one of the predominant C\textsubscript{3} species in the field site of this study, were found to be enriched in δ\textsuperscript{13}C following an altitudinal gradient at a rate of 2.68 ‰ km\textsuperscript{-1}, the highest rate among the evergreen species examined by Hultine and Marshall (1999). Körner et al., (1991) suggested that a decrease in both atmospheric pressure (specifically the decrease in oxygen partial pressure, where CO\textsubscript{2} assimilation increases due to reduced oxygen inhibition) and air temperature with altitude are responsible for this decrease in discrimination. Leaf discrimination may also be affected by stomatal closure induced by near freezing air temperatures at night, which are characteristic of high altitudes throughout most of the growing season (Hultine & Marshall, 2000; Kaufmann, 1982; Smith et al., 1984). Across the field site, elevation was strongly inversely correlated with atmospheric pressure (R\textsuperscript{2} = .20, p < .0001) and weakly inversely correlated with air temperature (R\textsuperscript{2} = .012, p < .001). The correlation with temperature should be interpreted with caution, as air temperature would increase sharply during the day and sites throughout the landscape were visited at random times. It is likely that the recorded air temperature at each site is more a reflection of the daily temperature gradient than the elevation gradient. As soil moisture is strongly inversely correlated with elevation in the site, the enrichment of δ\textsubscript{BULK} and δ\textsubscript{PROD} with the elevation gradient is also consistent with the Farquhar model of lower carbon isotope discrimination with decreasing plant water availability. Körner (2007) has cautioned against using regional data to generalize the relationship of altitude with moisture, as studies have shown that moisture gradients in different regions are very variable and may even be completely reversed in some areas, such as in Wang et al., (2010) where a significant positive relationship between soil moisture and altitude was observed, or in
arid areas, where leaf $\delta^{13}$C enrichment was observed at the lowest elevation, and precipitation was a stronger control of leaf $\delta^{13}$C than drought stress (Van de Water et al., 2002). Elevation was significantly positively correlated with both upland $\delta_{\text{PROD}}$ and riparian $\Delta_{\text{DIFF}}$ but soil moisture was not (Table 2.3), implying that other topographic attributes integrated into elevation may affect the spatial organization of $\delta_{\text{PROD}}$ and $\Delta_{\text{DIFF}}$. In the case of $\delta_{\text{PROD}}$ at the landscape level, this finding was corroborated by multiple regression analysis, where elevation was a significant predictor of all $\delta_{\text{PROD}}$ values in the landscape but soil moisture again was not (Table 2.8). The positive weight of elevation in the multiple regression model predicting $\delta_{\text{PROD}}$ matches the decreasing $C_3$ carbon discrimination gradient as explained previously. However, the multiple regression model was a weak predictor of landscape-scale $\delta_{\text{PROD}}$, and was not significant at all for landscape-scale $\delta_{\text{PROD}}$ values binned by soil depth used in calculation.

Soil moisture can affect the magnitude of $\Delta_{\text{DIFF}}$ two ways: through its negative effect on soil gas diffusivity (Penman, 1940) and its positive effect on the rate of biological CO$_2$ production until an optimum soil moisture value is reached (Kowalenko et al., 1978; Philips et al., 2010). As riparian $\Delta_{\text{DIFF}}$ was negatively correlated with soil TWI and UAA and soil moisture was a significant negative predictor of 50 cm $\Delta_{\text{DIFF}}$, this may be an indicator that the effect of soil moisture on gas diffusivity was a greater driver of $\Delta_{\text{DIFF}}$ than its effect on production. The two ways in which soil moisture can affect $\Delta_{\text{DIFF}}$ are also consistent with results of the multiple regression model showing the positive weight of elevation as a significant predictor of 50 cm $\Delta_{\text{DIFF}}$ (Table 2.9), as in this study, sites at higher elevations had less soil moisture and less CO$_2$ production.
Although flux was a strong significant positive predictor of $\delta_{\text{BULK}}$ at 50 cm and all $\delta_{\text{BULK}}$, this contradicted the study of Cerling et al. (1991), where $\delta_{\text{BULK}}$ has a negative relationship with soil flux, as mixing of atmospheric air with soil CO$_2$ increases as the magnitude of the flux decreases, resulting in more positive $\delta_{\text{BULK}}$ throughout the soil column.

Spatial Variation of Soil CO$_2$ Concentration and Flux

![Graph showing spatial variation of soil CO$_2$ concentration and flux](image)

**Figure 2.9. Plot-level Soil CO$_2$ Flux and Soil CO$_2$ Concentration Variation**

The variability of both soil CO$_2$ concentration and flux was higher in plots with higher average values (Figure 2.9). CO$_2$ concentration variability was highest in riparian plots, and also during weeks 1-3 in upland plots. As with soil $\delta^{13}$C-CO$_2$, the high variability of CO$_2$ in upland areas during weeks 1-3 may be due to the high soil moisture during the same time period. Soil moisture was positively correlated with CO$_2$ concentration and CO$_2$ flux in both riparian and upland areas (Table 2.3) and was a significant positive predictor of both CO$_2$ concentration at all depths and CO$_2$ flux.
(Tables 2.6 and 2.7). The positive relationship of both CO$_2$ concentration and flux with soil moisture has been previously attributed to be due the stimulation by soil moisture of heterotrophic and autotrophic soil CO$_2$ production (Kowalenko et al., 1978; Davidson et al., 2000). Models have shown that soil moisture generally enhances both soil CO$_2$ concentration and CO$_2$ flux, although at very high soil moisture levels both gas diffusivity and production can be inhibited (Davidson et al., 2000; Hashimoto and Komatsu, 2006). Elevation was negatively correlated with both upland CO$_2$ concentration and CO$_2$ flux and was a significant negative predictor of all CO$_2$ flux, all CO$_2$ concentrations, and CO$_2$ concentration at 20 cm and 50 cm. UAA, which is a strong indicator of watershed-scale CO$_2$ flux in the study site (Riveros-Iregui and McGlynn, 2008), was also positively correlated with riparian CO$_2$ flux and CO$_2$ concentration (Table 2.5), and a significant positive predictor of overall CO$_2$ flux (Table 2.5). The negative relationship of soil CO$_2$ flux with elevation has been attributed to higher soil temperature and soil moisture at lower areas of landscapes, which enhance CO$_2$ production through an increase in heterotrophic and autotrophic respiration and a higher amount of litter, soil organic matter, and fine root biomass (Allaire et al., 2012; Garrett & Cox, 1973; Kane et al., 2003). The negative relationship of soil CO$_2$ concentration with elevation observed in the study may be mediated by the decrease of soil moisture with elevation, as previous research by Amundson et al. (1989) in an area where soil moisture increases with elevation demonstrated that soil CO$_2$ concentration followed the soil moisture gradient and had a positive relationship with elevation.

**Temporal Variation of Soil Moisture, Soil $\delta^{13}$C-CO$_2$, Soil CO$_2$, and Soil CO$_2$ Flux**
Previous studies have noted that the increase of topographic control on soil moisture patterns during periods of moderate-high catchment wetness is highly probable (Famiglietti et al., 1998; Western et al. 1999; Jencso et al. 2009). Consistent with this, the significant inverse correlation of elevation with soil moisture, both overall and in upland areas, was highest in the first six weeks of the field season (Table 2.4). TWI was also significantly correlated with upland soil moisture during the first three weeks. UAA was not significantly correlated with upland soil moisture at any time and was only significantly correlated with soil moisture in riparian areas during the last three weeks of the field season, contradicting the of study Jencso et al. (2009) that the use of UAA to represent the lateral distribution of water in the same study site was most robust at the wettest state of the catchment.

The significant increase of upland $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ during the field season as soil moisture decreased (Figure 2.5) was consistent with previous studies, where soil $\delta_{\text{BULK}}$ and $\delta_{\text{PROD}}$ values were at their highest during dry periods (Ekblad & Högberg, 2001; Fessenden & Ehleringer, 2003; Flanagan et al., 1999). This seasonal variation was attributed to plant dynamic soil response to changes in environmental factors, resulting in fast cycling back to the atmosphere. Echoing the correlation between elevation and soil moisture, elevation and soil moisture were significantly related with soil $\delta^{13}\text{C-}\text{CO}_2$ only during the first six weeks of the field season (Table 2.4). Upland $\delta_{\text{BULK}}$ was negatively correlated with soil moisture and positively correlated with elevation during this time. The significant correlation of $\delta_{\text{BULK}}$ with soil moisture was not present in the multiple regression model (Table 2.7), which may have been affected by the strong correlation
between soil moisture and elevation. The non-significance of correlations and multiple regression models estimating δBULK and δPROD during weeks 7-9 may be due to the uniformity of soil moisture values at the end of the field season, as well as the emergence of evapotranspiration as a main control of soil moisture during dry periods. δPROD was positively correlated with elevation during weeks 1-6 and multiple regression models predicting δPROD at different depths during the same amount of time were significant, though their R^2 of the models was less than .1 (Table 2.8). The multiple regression model was less successful in predicting δPROD at specific depths. In contrast with both δBULK and δPROD, riparian ΔDIFF was negatively correlated with UAA and positively correlated with elevation during weeks 7-9 (Table 2.4). However, they were not significant predictors of any binned ΔDIFF value in the multiple regression model used. Soil moisture was a significant negative predictor of ΔDIFF only during isolated periods, and multiple regression models were not able to significantly predict a majority of binned ΔDIFF values (Table 2.7).

Field measurements of soil moisture were better related with the full seasonal variability of CO₂ concentration and flux compared to topographic attributes. Similar with soil δ¹³C-CO₂, CO₂ concentration and flux were negatively related with elevation during weeks 1-6, but were positively related to point soil moisture measurements throughout the entire duration of the season (Table 2.4). In fact, multiple regression models with soil moisture as the sole significant predictor performed best during weeks 7-9, explaining 24% of the variation of 5cm and 55% of 20 cm CO₂ concentration (Table 2.6). TWI and UAA were also significant positive predictors of CO₂ concentration and
flux at specific times in the season. TWI was a significant positive predictor of 20 and 50 cm CO₂ concentrations during weeks 1-3 (Table 2.6) while UAA was positively related with landscape-scale CO₂ flux during weeks 4-9, the only variable with which it had a consistent positive relationship (Table 2.5). TWI was also significantly correlated with riparian CO₂ flux during weeks 4-9, but the direction of the relationship was inconsistent (Table 2.4) and it was not a significant predictor of landscape-scale CO₂.

**SUMMARY AND CONCLUSIONS**

The stable carbon isotopic composition of CO₂ is altered during as CO₂ moves through the vegetation, soil, and atmosphere, and so has been studied as an indicator of changes in ecosystem CO₂ exchange. Soil moisture is an important factor in ecosystem CO₂ exchange through its influence on physiological and soil physical processes. However, the majority of previous research analyzing the influence of soil moisture on soil and soil-respired δ¹³C-CO₂ has been conducted with limited consideration of topographical variation, which controls the distribution of soil moisture across a landscape. This study linked the temporal and spatial variability of soil δ¹³C-CO₂, soil CO₂ concentration, and soil CO₂ flux measured at weekly to sub-weekly intervals during the growing season of a complex watershed to plot-level measurements of soil moisture and three topographic attributes, namely the Topographic Wetness Index (TWI), the Upslope Accumulated Area (UAA), and elevation.

Soil moisture and elevation were both significantly related to the spatial and temporal variability of soil δ¹³C-CO₂ in the watershed studied. In response to a soil moisture drydown, bulk soil δ¹³C-CO₂ and the calculated δ¹³C-CO₂ value of the
biological source in upland areas became more positive. This is consistent with the theoretical model of Farquhar et al. (1989) where plant $\delta^{13}\text{C-}\text{CO}_2$ increases with drought stress due to a decrease in photosynthetic discrimination, and has been observed previously at smaller scales. In contrast, soil $\delta^{13}\text{C-}\text{CO}_2$ did not change significantly in riparian areas, where soil moisture remained high throughout the field season. Elevation was positively correlated with soil $\delta^{13}\text{C-}\text{CO}_2$, following the negative gradient of soil moisture and atmospheric pressure with increasing elevation. Elevation and soil moisture were significantly correlated for two-thirds of the growing season when soil moisture was at medium-high levels, and elevation was a positive predictor of bulk soil $\delta^{13}\text{C-}\text{CO}_2$ during the same time period. Unlike elevation, TWI and UAA were not consistently significantly correlated with soil $\delta^{13}\text{C-}\text{CO}_2$. Plot soil moisture measurements were better predictors of soil CO$_2$ concentration and soil CO$_2$ flux than topographical attributes. This study indicates that in complex terrain at high to medium soil moisture levels, soil $\delta^{13}\text{C-}\text{CO}_2$ is linked to landscape position, possibly largely due to the influence of topographical heterogeneity on soil moisture distribution. Additional research is needed to further establish the control of topography on soil $\delta^{13}\text{C-}\text{CO}_2$ in other sites with complex terrain and at other times of the year.
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