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# Pulse Emissions of Carbon Dioxide during Snowmelt at a High-Elevation Site in Northern Arizona, U.S.A.

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## Abstract

The paradigm that winter is a dormant period of soil biogeochemical activity in high elevation or high latitude ecosystems has been amply refuted by recent research. Carbon dioxide (CO<sub>2</sub>) released from cold or snow-covered soil is a substantial component of total annual ecosystem carbon fluxes. Recent investigations have shown that the late-winter/early-spring transition is a period of high biogeochemical activity. However, little is known about the temporal dynamics of CO<sub>2</sub> from the snowpack itself during periods of snowmelt. We present a case study of three snowmelt events at a high-elevation site in northern Arizona during which we measured changes in CO<sub>2</sub> concentrations and fluxes above the snow and within the soil profile, and characterized the soil physical environment and site meteorological variables. We show that large pulses of CO<sub>2</sub> were emitted to the atmosphere during snowmelt, and we present evidence that these pulses came from CO<sub>2</sub> stored in snowpack. Earlier and more frequent snowmelts worldwide caused by climate change have the potential to alter the timing of release of CO<sub>2</sub> from land to atmosphere.

## Introduction

Over 60% of growing season carbon (C) uptake may be lost during the winter in high elevation or high latitude ecosystems as a result of carbon dioxide (CO<sub>2</sub>) efflux from snow-covered soil (Sommerfeld et al., 1993; Brooks et al., 1997; Monson et al., 2002; Brooks et al., 2004; Blankinship and Hart, 2012; Brooks et al., 2011), yet the dynamics and mechanisms of winter soil CO<sub>2</sub> efflux are not well understood. Snow insulates the soil from cold air temperatures, prevents the soil from freezing (Brooks et al., 1997), and allows soil biogeochemical activity to persist throughout the winter. The production of CO<sub>2</sub> in snow-covered soil is often attributed to decomposition of organic matter by cold-tolerant members of the heterotrophic microbial community (e.g., Sommerfeld et al., 1993, 1996; Brooks et al., 1996). However, the release of recently fixed plant C as CO<sub>2</sub> suggests that autotrophic plant root respiration may also contribute to soil CO<sub>2</sub> efflux from snow-covered soil (Grogan et al., 2001).

Biogeochemical activity in soil during the winter–spring transition may be significant. Plant-available nutrients may be more abundant during snowmelt than either before or after snowmelt (Brooks et al., 1998; Buckeridge and Grogan, 2010), and soil CO<sub>2</sub> efflux can be variable during the early spring (Liptzin et al., 2009; Buckeridge et al., 2010). Biogeochemical pulses during this period have been ascribed to freeze-thaw cycles, which lyse microbial biomass and physically disrupt soil organic matter. Soil heterotrophs that survived the freeze-thaw cycles are able to utilize the

mineral and organic nutrients in these new and more labile substrates. While studies have considered temporal dynamics of CO<sub>2</sub> efflux from snow-covered soil throughout the winter season (e.g. Musselman et al., 2005; Hubbard et al., 2005), little is known about CO<sub>2</sub> efflux dynamics during snowmelt.

Measurements of CO<sub>2</sub> efflux during snowmelt may be limited by the complexities of CO<sub>2</sub> gas transport in both soil and snow. Snow can act as a barrier to the diffusion of CO<sub>2</sub> from the soil to the atmosphere, resulting in increased CO<sub>2</sub> concentration in the snowpack and soil (Kelley et al., 1968). Furthermore, because snowpack density changes frequently, the volume of air-filled pore space in snow also changes (Seok et al., 2009). Ice layers in snow and rain-on-snow events have the potential to further complicate measurements of CO<sub>2</sub> efflux from snow.

Our understanding of CO<sub>2</sub> dynamics during snowmelt may be limited by currently available methods for estimating CO<sub>2</sub> fluxes from surfaces. Commonly used methods to measure CO<sub>2</sub> efflux from snow include measuring CO<sub>2</sub> concentration over time in a chamber located either on the snow surface (McDowell et al., 2000) or on the soil surface below the snowpack (McDowell et al., 2000; Hubbard et al., 2005), or measuring changes in the movement of CO<sub>2</sub> within snowpack with the diffusion-gradient technique (McDowell et al., 2000; Seok et al., 2009). However, a recent comparison of these methods found soil CO<sub>2</sub> efflux to vary by more than two orders of magnitude depending on the method used (Björkman et al., 2010). Estimates of CO<sub>2</sub> efflux during periods of melting snow are especially problematic using any of the above

methods because melting snow can change the concentration of CO<sub>2</sub> within snow and at the soil-snow boundary, as well as altering the diffusivity of gas in snow. However, given that The Intergovernmental Panel on Climate Change has identified the role of winter snow in ecosystems and its potential for future change as an area of interest (ACIA, 2005; Intergovernmental Panel on Climate Change, 2007), and that climate change may affect the magnitude, duration, timing, and number of snowmelt events, more information regarding dynamics of CO<sub>2</sub> flux during snowmelt is needed.

The use of two methods to measure CO<sub>2</sub> efflux concurrently can reduce the uncertainty associated with methodologies (Sullivan et al., 2010). Here, we describe a case study of CO<sub>2</sub> dynamics both during the presence of snow and during three snowmelt events at a high-elevation site in northern Arizona, U.S.A. By using two methods with high temporal resolution, one located below the snow surface measuring soil CO<sub>2</sub> efflux and the other above the snow surface measuring ecosystem CO<sub>2</sub> fluxes, we show CO<sub>2</sub> efflux dynamics during snowmelt. We provide evidence that CO<sub>2</sub> stored in the snowpack is rapidly released to the atmosphere during snowmelt.

## Methods

### STUDY SITES

We measured CO<sub>2</sub> efflux in March 2006 at a site in northern Arizona that burned severely in 1996. This site, located 29 km north-northwest of Flagstaff, Arizona, has been described in detail elsewhere (Dore et al., 2008, 2010; Montes-Helu et al., 2009; Sullivan et al., 2010, 2011), but here we provide a brief description of pertinent site characteristics. The 1996 fire killed all the trees within the study area and resulted in a vegetation conversion of the ponderosa pine (*Pinus ponderosa* C. Lawson var. *scopulorum* Engelm.) forest to a mostly perennial grassland. In 2006, peak-season projected leaf area index was 0.6 m<sup>2</sup> m<sup>-2</sup> and was comprised entirely of understory plants. The soil is classified as a Mollic Eutroboralf and the soil A horizon (0–7 cm) textural class is a silt loam. The fire consumed nearly all the O horizon (Sullivan et al., 2011). More detailed soil characteristics are available in Dore et al. (2008, 2010).

The site is located at an elevation of 2270 m. As a result, the site experiences cold winters with substantial snowfall in most years. Average 1971–2000 total annual precipitation was 563 mm y<sup>-1</sup> (Western Regional Climate Center, <http://www.wrcc.dri.edu/index.html>), of which roughly half was snow (Sheppard et al., 2002). In 2006, total annual precipitation was 516.7 mm (Dore et al., 2008). Average air temperature in 2006 at 3 m above the ground was 8.5 °C, while the minimum and maximum temperatures were –17.6 and 30.1 °C, respectively. Meteorological sensors at the sites indicated that both January and February 2006 were mild and dry, with little precipitation falling until March, when substantial snow fell over the course of several weeks.

### SOIL CO<sub>2</sub> CONCENTRATIONS AND SOIL CO<sub>2</sub> EFFLUX MEASUREMENTS AT THE MINERAL SOIL SURFACE

We buried solid-state infra-red gas analyzer (IRGA) probes (GMM 222; Vaisala Inc., Helsinki, Finland) at different depths in the soil profile to continuously measure CO<sub>2</sub> concentrations. Sulli-

van et al. (2010) described this method in detail, which is based on Tang et al. (2003); here, we provide a brief description of the methodology. When connected to a power source, datalogger (CR10xTD, Campbell Scientific Inc., Logan, Utah, U.S.A.), and multiplexer (AM25T, Campbell Scientific, Inc.), these probes measured CO<sub>2</sub> concentrations every 20 s, which generated 30 min averages stored in the CR10xTD. We buried three sets of GMM 222 probes, with each set consisting of three GMM 222 probes placed at 2, 10, and 20 cm below the mineral soil surface. To protect the GMM 222 probes from water damage, we shrouded each probe with a commercially available in-soil adaptor (211921GM, Vaisala) and sealed the adaptor to the probe with inert silicone grease. We measured volumetric soil water content within 20 cm of each GMM 222 at each depth using horizontally buried ECH<sub>2</sub>O probes (Decagon Devices, Pullman, Washington, U.S.A.). We developed site-specific calibrations for the ECH<sub>2</sub>O probes to accurately estimate water content and to correct for the effect of temperature on the probes (Montes-Helu et al., 2009). We measured soil temperature adjacent to each GMM 222 probe using a thermocouple attached to the CR10xTD datalogger. For both the thermocouples and the ECH<sub>2</sub>O probes, measurements were taken every 20 s and were recorded as 30 min averages.

We estimated CO<sub>2</sub> efflux using Fick's first law, an estimate of soil diffusivity, and the measured CO<sub>2</sub> profile concentrations in the mineral soil taken every 30 min. To estimate the soil gas diffusion coefficient, we applied a model developed by Moldrup et al. (1999), described in detail for this application by Tang et al. (2005) and Sullivan et al. (2010). The Moldrup et al. (1999) model of soil gas diffusion uses measurements of the total soil porosity, air-filled porosity, clay fraction, and the molecular diffusivity of CO<sub>2</sub> in air to calculate the rate of movement of CO<sub>2</sub> through soil from zones of high concentration at depth to zones of low concentration near the surface. Soil CO<sub>2</sub> efflux measured with the soil CO<sub>2</sub> diffusion gradient method during the growing season was validated by a strong correlation ( $r^2 = 0.80$ ) to high-quality nighttime measurements of CO<sub>2</sub> using eddy covariance at this site (Sullivan et al., 2010).

### EDDY COVARIANCE MEASUREMENTS

We used the eddy covariance method to measure ecosystem-level CO<sub>2</sub> fluxes at this site. The eddy covariance tower was located 150 m north of the soil CO<sub>2</sub> efflux measurements. Eddy covariance has been previously used to measure soil CO<sub>2</sub> efflux in different ecosystems (e.g., Janssens et al., 2000; Baldocchi et al., 2006; Richardson et al., 2006; Jassal et al., 2007; Sullivan et al., 2010). Precautions must be taken to avoid confounding soil CO<sub>2</sub> efflux with aboveground plant respiration and photosynthesis. These precautions include using only nighttime data, setting the eddy covariance instruments below the forest canopy, or using eddy covariance at sites with little vegetation. In the present study, the instruments were close to the ground (3 m) and vegetation was sparse (maximum growing season leaf area index was 0.6 m<sup>2</sup> m<sup>-2</sup> and 40% of the cover was bare soil; Montes-Helu et al., 2009). Additionally, low air and soil temperatures, snowpack, and lack of perennial vegetation resulted in negligible plant photosynthetic activity during the day in winter (Dore et al., 2008). However, to be conserva-

tive in our use of eddy covariance to measure soil CO<sub>2</sub> efflux, we compare only nighttime values and excluded low-quality data, determined by quality flagging using the CarboEurope methodology (steady-state test and integral turbulence characteristic test; Foken and Vichura, 1996). Like the soil CO<sub>2</sub> diffusion gradient method, the eddy covariance tower recorded 30 min averages of CO<sub>2</sub>, water, and energy fluxes from land to atmosphere. Dore et al. (2008 and 2010) and Montes-Helu et al. (2009) provide in-depth descriptions of the eddy covariance measurements, but we summarize relevant instrumentation below.

To measure ecosystem fluxes of CO<sub>2</sub>, H<sub>2</sub>O, and energy, we used a closed-path IRGA (Li-7000, LI-COR, Lincoln, Nebraska, U.S.A.) and a three-dimensional sonic anemometer (CSAT3, Campbell Scientific) positioned 3 m above the ground. A pump (N89, KNF Newberger, Freiburg, Germany) drew air through 9 m of Teflon tubing between the sonic anemometer and the Li-7000 at a rate of 10 L min<sup>-1</sup>. Data were acquired at 20 Hz by a datalogger (CR1000, Campbell Scientific) and custom-made software (G. Manca, JRC Italy) applying coordinate rotations, linear detrending, and calculating quality flags (see above) on the 30 min averages (Foken and Vichura, 1996). We measured the albedo of the site surface using a CNR1 (Kipp and Zonen, Delft, The Netherlands) radiometer. We report measurements of albedo during the hours 9:00 to 16:00 when the sun was highest in the sky. We measured air temperature and precipitation using a WXT510 (Vaisala) weather station. Soil temperature and soil water content at the eddy covariance tower were measured at 10 cm below the mineral soil surface using a TCAV thermocouple (Campbell Scientific) and ECH<sub>2</sub>O probes, respectively. We calculated soil heat flux (*G*; described by Montes-Helu et al., 2009) at 8 cm below the mineral soil surface using a HFP01SC (Hukseflux, Delft, The Netherlands) soil heat flux probe.

#### IDENTIFICATION OF SNOWMELT EVENTS

We do not have a record of snow depth at this site during March 2006, and thus we used two approaches to identify snowmelt events. The first consisted of using soil physical and meteorological changes associated with snow. Changes in microclimate and energy fluxes associated with periods of snowmelt are well documented (Weller et al., 1972; Ling and Zhang, 2003) and may be used to predict snowpack dynamics (Ling and Zhang, 2003). Other studies have inferred snowmelt from changes in microclimate or energy balance, including Harte et al. (1995), who simply defined snowmelt as having occurred when soil temperatures 5 cm deep equaled +1 °C. Our approach incorporates several changes in both microclimate and energy fluxes to accurately capture snowmelt dynamics. The first requirement for a snowmelt event to have occurred was the presence of snow on the ground prior to the event. When snow was on the ground, albedo was substantially higher than when no snow was present. The second requirement of a snowmelt event was air temperatures greater than 0 °C. Once these two requirements were met, we further identified snowmelt events by a decline in albedo, and an increase in latent heat, soil water content, and *G*. The second approach we used to identify snowmelt events incorporated data from a SNOTEL (<http://www.wcc.nrcs.usda.gov/snow>) station located in Fry Canyon, 42 km distant from the site and only 75 m lower in elevation. In northern Arizona, elevation

strongly influences temperature (Sheppard et al., 2002), which in this case may affect snowpack dynamics by changing the location of the rain/snow boundary. We use these data only to corroborate the patterns of snowmelt we observed at our site because of potential site-specific meteorological differences between the SNOTEL station and our site.

#### STATISTICAL ANALYSIS

Our goal with this case study was to report the occurrence and magnitude of CO<sub>2</sub> efflux from snow-covered soil during periods of snowmelt. We report these data from only one site, which had three soil CO<sub>2</sub> diffusion gradient profiles and one eddy covariance tower. As a result, we have little or no spatial replication, our measurements were not independent of each other, and in some cases the data were non-normally distributed. Additionally, our study design did not allow a comparison of CO<sub>2</sub> fluxes from snow-covered soil that was not experiencing snowmelt during the same period that snowmelt occurred. Therefore, we used a variety of graphical approaches to elucidate the dynamics of CO<sub>2</sub> efflux during snowmelt, but we did not use parametric statistics.

## Results and Discussion

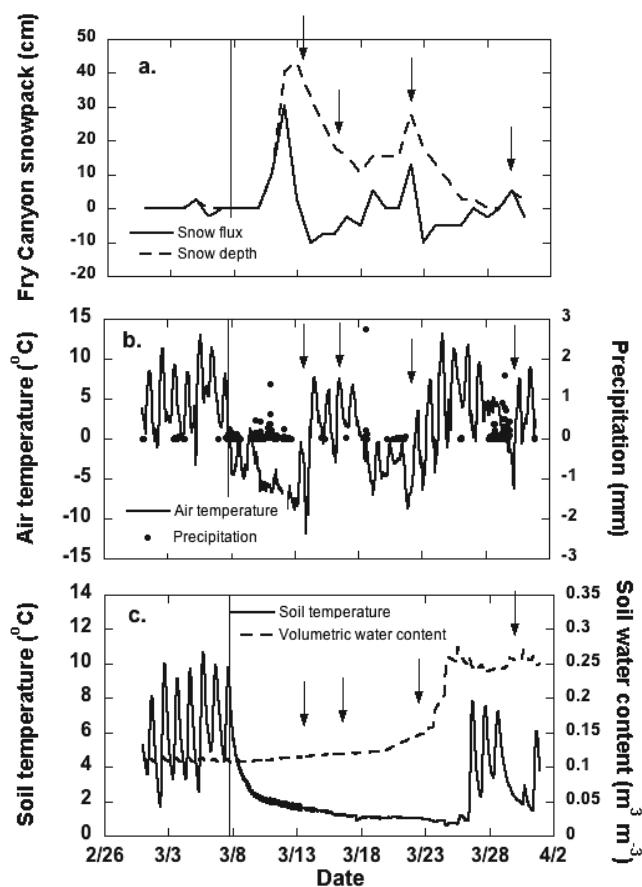
#### SNOWPACK AND SNOWMELT EFFECTS ON THE PHYSICAL ENVIRONMENT

We identified three major snowfall and snowmelt events at our site based on energy fluxes and meteorology. The first snowfall began at 19:40 on 7 March (depicted as the vertical line in Figs. 1, 2, and 3) and continued, heavily at times, until 12 March. Another snowfall event occurred on the night of 18 March, as another cold front moved across northern Arizona (Fig. 1, Part b). A third storm system brought heavy precipitation on 28 through 30 March that consisted of a rain/snow mix.

We identified three large snowmelt events that followed these snowfall events. The first snowmelt event began on 14 March when temperatures reached 8 °C for the first time since snow fell on 7 March, and continued until 18 March. The second snowmelt event began on 22 March when daytime temperatures rose above freezing for the first time since 18 March. The third snowmelt event began on 30 March when the cold front that caused the precipitation on 28 through 30 March moved out of the region and warmer temperatures returned (Fig. 1, Parts a and b).

The Fry Canyon SNOTEL station provided a useful reference for our estimation of snowfall and snowmelt events (Fig. 1, Part a). However, snow accumulated earlier at our site than at the Fry Canyon SNOTEL site. After 12 March, the trends of snowpack dynamics at the two sites were similar throughout the rest of the month. We calculated the daily flux of snow (the net change in snow depth, expressed as cm d<sup>-1</sup>) at the Fry Canyon SNOTEL station in order to more effectively depict snowpack dynamics at our site during March 2006 (Fig. 1, Part a).

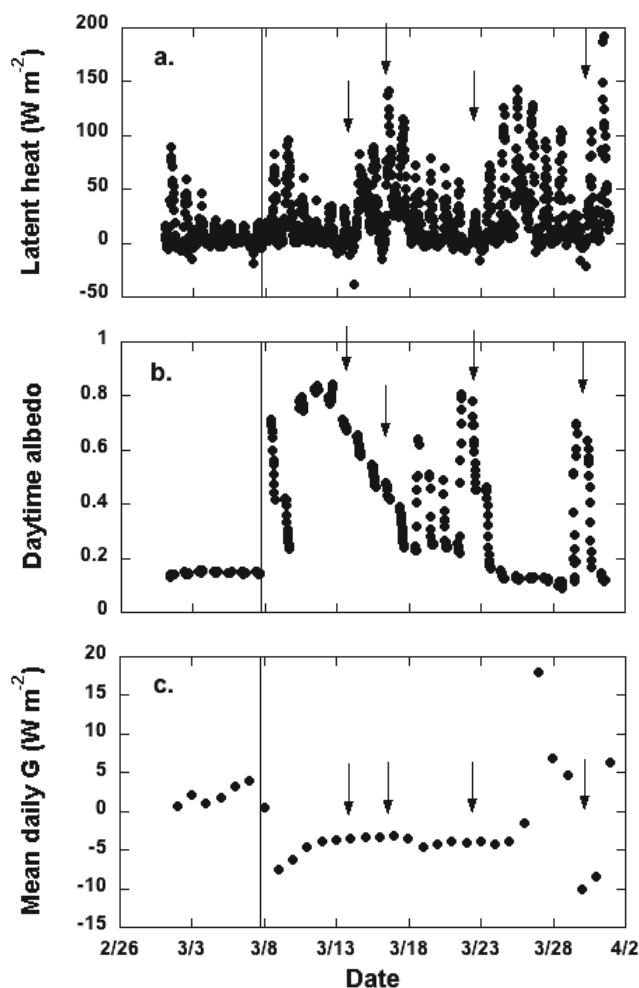
The soil physical environment was strongly affected by the presence of snow. Soil temperatures at 10 cm below the mineral soil surface reflected the presence of snowpack; diel variation, which had been as large as 8 °C before snowpack, disappeared while the soil was covered with snow (Fig. 1, Part c). Soil temperatures steadily declined below 1 °C by 26 March when diel variation



**FIGURE 1.** March 2006 snowpack dynamics and soil meteorological conditions. (a) Daily snowpack depth and flux (the net change in snow depth, expressed as  $\text{cm d}^{-1}$ ) measured at the Fry Canyon SNOTEL station located 42 km south from and 75 m lower in elevation than the eddy covariance site. (b) Total half-hour precipitation and mean half-hour air temperature measured at the eddy covariance tower in March 2006. (c) Mean half-hour soil temperature and soil volumetric water content at the eddy covariance tower measured 10 cm below the mineral soil surface from February to April 2006. In all panels, the vertical line on 7 March indicates the beginning of snowfall; dark arrows indicate the beginning of the four pulses of carbon dioxide ( $\text{CO}_2$ ) observed during snowmelt.

returned. On the other hand, soil volumetric water content 10 cm below the mineral soil surface was not different before and after snowfall, but began steadily increasing after snowmelt on 14 March. The 22 March snowmelt event caused an immediate increase in soil water content from  $0.16$  to  $0.26 \text{ m}^3 \text{ m}^{-3}$  (Fig. 1, Part c). Interestingly, the 30 March snowmelt event did not have a large effect on soil water content. The soil was already near saturation as measured by the maximum volumetric water content observed during 2006 (Dore et al., 2008), but it is also possible that the snowmelt event on 30 March was not as large a source of water as the previous snowmelt event.

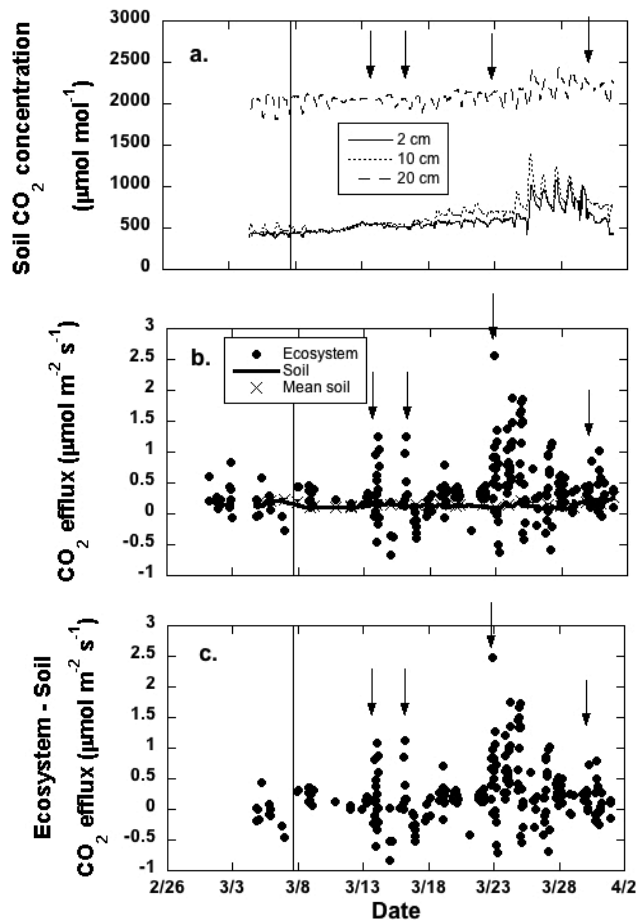
The latent heat at the site increased during each snowmelt event described above (Fig. 2, Part a). During the snowmelt event that began on 14 March, the latent heat increased in a stepwise fashion: first on 14 March, and again on 16 March. The next major increase in latent heat began 23 March, immediately after snowmelt began on 22 March and continued for several days. The final in-



**FIGURE 2.** Energy fluxes at the eddy covariance site during March 2006. (a) Mean half-hour latent heat measured at the eddy covariance tower from February to April 2006. (b) Mean half-hour albedo measured at the eddy covariance tower between the hours of 09:00 and 16:00 from February to April 2006. (c) Mean daily soil heat flux (G) at the eddy covariance tower measured 8 cm below the mineral soil surface from February to April 2006. In all panels, the vertical line on 7 March indicates the beginning of snowfall; dark arrows indicate the beginning of the four pulses of carbon dioxide ( $\text{CO}_2$ ) observed during snowmelt.

crease in latent heat occurred on 28 March. These increases in latent heat were the result of increases in soil water, which increased the amount of water available for evaporation.

The albedo at the site increased substantially over background levels ( $\sim 0.15$ ) to a maximum (0.84) on 12 March after snow accumulated (Fig. 2, Part b). Immediately following each of the snowmelt events on 14, 22, and 30 March, albedo declined. Much, but not all, of the snow melted during the snowmelt event that began 14 March and continued until 18 March, because the albedo dropped to 0.24 on 18 March. As snow melted, more vegetation and dead, fallen trees from the fire were exposed, reducing the albedo. It is important to note that based on albedo alone, it would appear that all snow had melted from the site by 24 March. However, soil temperature (Fig. 1, Part c) and G values (see below) suggest that snow was completely lost on or around 26 March.



**FIGURE 3.** Carbon dioxide ( $\text{CO}_2$ ) concentrations and fluxes during March 2006. (a) Mean half-hour soil  $\text{CO}_2$  concentration at 2, 10, and 20 cm below the mineral soil surface measured using three soil  $\text{CO}_2$  diffusion gradient profiles in March 2006. Presented values are the means of three profiles. (b) Mean half-hour  $\text{CO}_2$  fluxes during the night measured using the soil  $\text{CO}_2$  diffusion gradient method (solid black line), daily mean soil  $\text{CO}_2$  efflux values from each of the three profiles ( $\pm$  one standard error,  $n = 3$ ; indicated by X's), and mean half-hour ecosystem-level  $\text{CO}_2$  fluxes (medium and high quality data only; see Methods) during the night measured using eddy covariance (black circles) in March 2006. Low soil  $\text{CO}_2$  fluxes led to narrow error bars (when viewed at this scale) associated with daily mean soil  $\text{CO}_2$  efflux. (c) Ecosystem-level  $\text{CO}_2$  fluxes measured with eddy covariance minus soil  $\text{CO}_2$  efflux measured with the diffusion gradient profiles. A value of zero occurred when soil  $\text{CO}_2$  efflux accounted for all the ecosystem-level  $\text{CO}_2$  efflux measured by eddy covariance. In all panels, the vertical line on 7 March indicates the beginning of snowfall; dark arrows indicate the beginning of the four pulses of carbon dioxide ( $\text{CO}_2$ ) observed during snowmelt.

Average daily  $G$  was a good indicator of the duration and depth of snow cover (Fig. 2, Part c). Before snow fell on 7 March, average daily  $G$  values were positive ( $2.1 \text{ W m}^{-2}$ ), indicating inputs of energy to the soil from solar radiation. However, after the snow fell, the average  $G$  on 8 March was sharply negative ( $-7.5 \text{ W m}^{-2}$ ). Increasing average daily  $G$  values on 26 and 27 March indicated that these were the first truly snow-free days since snow first accumulated on 7 March. All snow melted on 30 March and the average daily  $G$  value for 31 March was positive again.

Soil  $\text{CO}_2$  concentrations were generally lowest 2 cm below the mineral soil surface, slightly higher at the 10 cm soil depth, and highest at the 20 cm soil depth (Fig. 3, Part a). In the days immediately after snow fell on 7 March, the  $\text{CO}_2$  concentrations at the 2 and 10 cm depths were nearly equal. There are both physical and biological explanations for this result. The snowpack acted as a barrier to diffusion of  $\text{CO}_2$  out of the soil because of both the physical resistance of the snow and alteration of the diffusion gradient created by  $\text{CO}_2$  contained within the snowpack. Additionally, comparable soil temperature and water content at 2 and 10 cm depth may have resulted in similar rates of biological activity, resulting in similar production of  $\text{CO}_2$  at 2 and 10 cm depths. Either of these mechanisms could have caused  $\text{CO}_2$  concentrations at the 2 cm depth to rise above concentrations that existed when no snow was present. Soil  $\text{CO}_2$  concentrations remained at  $\sim 500 \mu\text{mol mol}^{-1}$  at both the 2 cm and 10 cm depths until 26 March, approximately the time when the soil surface was free of snow, and  $\text{CO}_2$  concentrations roughly doubled. This was likely due to greater heterotrophic activity in response to inputs of heat from solar radiation (as shown by increased  $G$  and soil temperature) and increases in soil water content.

Soil  $\text{CO}_2$  efflux at the mineral soil surface, whether snow was present or not, was low in March 2006. The largest single half-hour average flux was  $0.4 \mu\text{mol m}^{-2} \text{ s}^{-1}$  and occurred on 25 March after soil  $\text{CO}_2$  concentrations increased (Fig. 3, Part b). Soil  $\text{CO}_2$  efflux followed the trend of soil temperature in that both diel variation and absolute values declined under snowpack. However, soil  $\text{CO}_2$  efflux responded more rapidly to the melting event that began 22 March than soil temperature; its response was more similar to changes in soil water content. Both soil temperature and soil water content have previously been shown to significantly affect soil  $\text{CO}_2$  efflux at this site (Sullivan et al., 2010, 2011). The snowpack insulated the soil environment from air temperatures that reached  $-10 \text{ }^\circ\text{C}$ ; as a result, the activity of the soil heterotrophic community likely persisted but at a level below that during the warmer soil temperatures experienced before the storm on 7 March. The warmer and wetter soil conditions created by the 22 March snowmelt event likely increased the activity of the heterotrophic community. While it is possible that autotrophic respiration contributed to some of the soil  $\text{CO}_2$  efflux we measured both under snowpack and during snowmelt (Grogan et al. 2001), evidence from soil  $\text{CO}_2$  efflux during the growing season at this site indicated that the wildfire caused an increase in the relative contribution of heterotrophic respiration to soil  $\text{CO}_2$  efflux (Sullivan et al., 2011). This shift was attributed to the lower abundance of fine roots in burned than unburned soil 10 years after the fire.

Nighttime  $\text{CO}_2$  fluxes measured with the eddy covariance technique were much more variable than nighttime  $\text{CO}_2$  efflux measured at the mineral soil surface with the soil  $\text{CO}_2$  diffusion gradient method (Fig. 3, Part b). Specifically, we observed four large pulses of  $\text{CO}_2$  from the ecosystem after the accumulation of snowpack on 7 March. These four large pulses of  $\text{CO}_2$ , defined as two or more fluxes greater than  $0.5 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , occurred during the snowmelt events described above (arrows in all figures denote timing of pulses). Interestingly, the largest of the four pulses coincided with the melting event that began 22 March. This pulse not

only had the highest single measurement of nighttime CO<sub>2</sub> efflux during March ( $\sim 2.5 \mu\text{mol m}^{-2} \text{s}^{-1}$ ), but it also had the greatest duration, persisting each night from 23 to 25 March. The 22 March melting event was the first snowmelt event that resulted in the complete loss of snow several days later from the site as depicted by changes in energy fluxes such as  $G$  and the return of diel variation in soil temperature.

Pulses of soil CO<sub>2</sub> efflux from the mineral soil do not explain the pulses of CO<sub>2</sub> we measured using eddy covariance (Fig. 3, Part c). The difference between these two methods of measuring CO<sub>2</sub> fluxes was substantial during these pulse events (Fig. 3, Part c). Several lines of evidence suggest that the substantial difference between pulses of CO<sub>2</sub> measured by eddy covariance and soil CO<sub>2</sub> efflux during snowmelt events (Fig. 3, Part c) were caused by the release of CO<sub>2</sub> from the snowpack during melting. First, each of the four CO<sub>2</sub> pulses measured by eddy covariance occurred during snowmelt events. The first two pulses occurred during the melting event that began 14 March and lasted until 18 March. As described above, the third pulse, which was the largest in both magnitude and duration, began and continued during the 22–26 March snowmelt period. The fourth pulse coincided with the 30 March snowmelt event. Second, the CO<sub>2</sub> in the pulses did not come from an exogenous source and are not attributable to sources in the ecosystem other than soil. The cumulative CO<sub>2</sub> efflux measured using eddy covariance between 3 and 31 March was  $23.5 \text{ g m}^{-2}$ . The cumulative CO<sub>2</sub> efflux between those dates measured using the soil diffusion gradient technique was  $18.9 \text{ g m}^{-2}$ , a difference of only 20%, suggesting that the CO<sub>2</sub> measured at the eddy covariance tower largely originated from soil. Aboveground respiration rates were low at this site even during warm and wet seasons (Dore et al., 2008). Aboveground woody debris (largely stems and branches of trees killed by the fire) comprised 43% of the total C stock on site, but the decomposition rate of this large pool only contributed 16% of the total yearly ecosystem respiration (Dore et al., 2008). Given that these pulses occurred at relatively low temperatures during our winter measurements compared to the growing season, we cannot attribute this CO<sub>2</sub> to other sources within the ecosystem. Third, though the CO<sub>2</sub> that constituted the pulses was originally derived from soil, there were no pulses of soil CO<sub>2</sub> efflux or large changes in soil CO<sub>2</sub> concentration that explain the pulses we observed with the eddy covariance technique (Fig. 3, Parts a and b). If there were such pulses of soil CO<sub>2</sub> efflux, the difference between CO<sub>2</sub> flux measured using eddy covariance and soil CO<sub>2</sub> efflux at the soil surface would be close to zero (Fig. 3, Part c). An advantage of the soil CO<sub>2</sub> diffusion gradient method is that it uses changes in soil CO<sub>2</sub> concentrations, soil temperature, and soil water content at three depths in the soil to estimate CO<sub>2</sub> flux. If snowmelt had changed any one of these factors in a manner that would have caused a pulse emission of CO<sub>2</sub> from soil, the soil CO<sub>2</sub> diffusion gradient method should have measured a pronounced increase in CO<sub>2</sub> efflux. For instance, if water from melting snow had caused these pulses by flushing CO<sub>2</sub> out of air-filled soil pore space, our high-resolution measurements of soil CO<sub>2</sub> concentrations and soil water content would have captured this flux. Furthermore, though soil CO<sub>2</sub> efflux had high spatial variability at this site during the growing season (Sullivan et al., 2010), the eddy covariance technique integrated fluxes over a 1 km<sup>2</sup> area, and the low rates of soil

CO<sub>2</sub> efflux measured during March 2006 had low spatial variability (indicated by narrow error bars in Fig. 3, Part b). It is therefore unlikely that these pulses originated from within the soil.

Largely due to methodological constraints and the transient nature of snowmelt events, there is a paucity of research describing ecosystem processes during snowmelt (but see Friberg et al., 1997; Brooks et al., 1998; Buckeridge and Grogan, 2010). Friberg et al. (1997) described pulse emissions of CO<sub>2</sub> and methane during snowmelt using eddy covariance, yet they lacked the high temporal resolution measurements of soil gas flux under melting and undisturbed snowpack we show in the present study to conclusively eliminate soil gas production during snowmelt. Though our study was limited to a single site in northern Arizona that experienced three large snowmelt events during the month of our measurements, we measured large fluxes of CO<sub>2</sub> during snowmelt. The most logical explanation for these pulses is that they were the result of CO<sub>2</sub> released from snowpack during melting events. Our study included measurements of soil and ecosystem CO<sub>2</sub> fluxes as well as energy fluxes and meteorological conditions at a high temporal resolution during periods of snowpack and snowmelt. In this case study, we cannot provide evidence that these pulses occur in other ecosystems, though based on Friberg et al. (1997), it seems reasonable to speculate that they may. If so, such pulses occurring over large areas may affect the temporal dynamics of CO<sub>2</sub> fluxes between the land and the atmosphere. Arctic and alpine regions are experiencing earlier snowmelt as a result of warmer spring temperatures associated with climate change (Solomon et al., 2007). Additionally, mountain regions are experiencing an increase in mid-winter thawing events and less winter precipitation falling as snow (Rikiishi et al., 2004; Scherrer et al., 2004; Mote et al., 2005). This study presents additional evidence that ecosystem processes during periods of snowmelt are dynamic and need to be explored more thoroughly.

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