

# Snowpack-atmosphere gas exchanges of carbon dioxide, ozone, and nitrogen oxides at a hardwood forest site in northern Michigan

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## Abstract

Snowpack-atmosphere gas exchanges of  $CO_2$ ,  $O_3$ , and  $NO_x$  (NO + NO<sub>2</sub>) were investigated at the University of Michigan Biological Station (UMBS), a mid-latitude, low elevation hardwood forest site, during the 2007-2008 winter season. An automated trace gas sampling system was used to determine trace gas concentrations in the snowpack at multiple depths continuously throughout the snow-covered period from two adjacent plots. One natural plot and one with the soil covered by a Tedlar sheet were setup for investigating whether the primary source of measured trace gases was biogenic (i.e., from the soil) or non-biogenic (i.e., from the snowpack). The results were compared with the "White on Green" study conducted at the Niwot Ridge (NWT) Long Term Ecological Research site in Colorado. The average winter  $CO_2$  flux ± s.e. from the soil at UMBS was  $0.54 \pm 0.037 \,\mu$ mol m<sup>-2</sup> s<sup>-1</sup> using the gradient diffusion method and  $0.71 \pm 0.012 \,\mu$ mol m<sup>-2</sup> s<sup>-1</sup> using the eddy covariance method, and in a similar range as found for NWT. Observed snowpack-O3 exchange was also similar to NWT. However, nitrogen oxides (NO2) fluxes from snow at UMBS were 10 times smaller than those at NWT, and fluxes were bi-directional with the direction of the flux dependent on NO<sub>x</sub> concentrations in ambient air. The compensation point for the change in the direction of NO<sub>x</sub> flux was estimated to be 0.92 nmol mol<sup>-1</sup>. NO, in snow also showed diurnal dependency on incident radiation. These NO<sub>v</sub> dynamics in the snow at UMBS were notably different compared to NWT, and primarily determined by snow-atmosphere interactions rather than by soil NO<sub>x</sub> emissions.

## Introduction

Winter historically has been perceived as a period of suppressed biogeochemical activity (Campbell et al., 2005). It was assumed that trace-gas exchange between the soil and the atmosphere halted with snow cover or when soil temperatures dropped to below 0°C (Steudler et al., 1989; Bouwman, 1990). However, it was discovered later that  $CO_2$  concentrations were elevated at the bases of snowpack at high latitude or high elevation sites (Kelley et al., 1968; Coyne and Kelley, 1971; Solomon and Cerling, 1987), which was indicative of continued biological activity even during snow cover with soil temperatures near 0°C (Taylor and Parkinson, 1988; Sommerfeld et al., 1991). Subsequent and recent studies showed that elevated  $CO_2$  concentration in the snowpack are not limited to high latitude or high elevation sites. These studies also showed how snow insulates the soil from sub-freezing ambient air temperatures (Groffman et al., 2001), that microbial activity under snow can stay active until soil temperatures reach below -5°C (Brooks et al., 2005), and that soil microbial communities during snow cover can be different from the growing season (Monson et al., 2006b). These findings challenged the traditional view of winter with respect to the annual biogeochemical cycle.

As the recognition grew that wintertime processes can make important contributions to the annual biogeochemical budget, the number of flux measurements during the snow-covered season increased for

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different natural ecosystems. For instance, measurements were made at high latitude tundra and permafrost sites (Zimov et al., 1996; Fahnestock et al., 1998; Welker et al., 2000), at high elevation alpine and subalpine sites (Sommerfeld et al., 1993; Brooks et al., 1996; Williams et al., 1998; Schurmann et al., 2002; Monson et al., 2006a; Schindlbacher et al., 2007; Bowling et al., 2008; Liptzin et al., 2009), and at low elevation, agricultural and forested sites (van Bochove et al., 1996; Alm et al., 1999; Groffman et al., 2001; Maljanen et al., 2007). Result from these measurements indicated that a large percentage (as much as 60%) of growing season carbon uptake can be lost during the winter, emphasizing the importance of trace gas exchange through snow for ecosystem functioning and annual biogeochemical budgets (Sommerfeld et al., 1993; Monson et al., 2005; Schindlbacher et al., 2007).

The aforementioned studies examined stable greenhouse gases, i.e., CO<sub>2</sub> and N<sub>2</sub>O, with little attention given to reactive gases. From the atmosphere and climate perspective, knowing how reactive trace gases might interact with snow is vital as these gases influence the oxidation capacity of the atmosphere and ozone  $(O_3)$ formation. From the ecological perspective, reactive trace gases, for instance nitrogen oxides, have an important function in various biogeochemical processes such as by influencing the nutritional balance of terrestrial ecosystems (Sparks et al., 2003; Lockwood et al., 2008; Nave et al., 2009) and acid deposition (Schulze et al., 1989). Trace gas exchange studies conducted in the Polar Regions showed that snow is a highly reactive medium for photochemical reactions, heterogeneous reactions, and physical exchange processes (Grannas et al., 2007; Simpson et al., 2007; Domine et al., 2008). As a result, snow could have an important impact on the overlying atmosphere. For example, complete depletion of ambient  $O_3$  has been observed over the snowpack in the polar coastal regions (Simpson et al., 2007), while at the South Pole, a doubling in ambient O<sub>3</sub> concentration was seen in the atmospheric surface layer (Helmig et al., 2008). At forested sites, the fate of nitrate – an important source for nitrogen for plants – in the winter is complicated by snow, as it serves as a medium for facilitating the temporal storage and mobilization of deposited nitrate (Brooks and Williams, 1999) and a chemical substrate for photochemical conversion of nitrate to nitrogen oxides  $(NO_x)$  (Honrath et al., 2000a).

Another motivation is to improve our understanding how declining snowpack due to the changing climate will affect trace gas exchange in the winter. Future climate scenarios are predicting less snow and more summer rain (Barnett et al., 2005). In the past 50 years, the Western U.S., for instance, has experienced reductions in snowpack (Mote et al., 2005; Hamlet et al., 2005) and higher springtime temperatures (Aguado et al., 1992; Kalra et al., 2008). It is likely that the decline in snowpack will result in modification to plant and microbial metabolism and distribution (Groffman et al., 2001), ultimately changing the biogeochemical cycle.

The most comprehensive study to date on gas fluxes in snow-covered ecosystems was conducted at the Niwot Ridge (NWT) Long Term Ecological Research site in Colorado (Williams et al., 2009). This study included measurements of the stable greenhouse gases  $CO_2$  and  $N_2O$ , as well as the more reactive gases  $NO_{x3}$ ,  $O_3$ , and volatile organic compounds (VOCs), and emphasized both the role of biological activity under the snowpack and chemical reactions within the snowpack. We collected similar measurements at a low elevation site with two goals in mind. One is determining if the results from NWT apply at sites with different snowpack characteristics. The other is to predict how "at-risk" snow can potentially alter the fluxes of trace gases through snow. Here, "at-risk" snow is defined as current snow that is at or near the melting phase during mid-winter conditions. With climate change, "at-risk" snow would melt and not accumulate but precipitation would occur as rain instead. Along the same latitudinal zone, low elevation sites in general have warmer wintertime air temperatures than at high elevation sites. Snow at low elevation sites would be "at-risk", and thus, low elevation sites can serve as proxies to future snow conditions at high elevations.

In this study, we measured trace gases in the snowpack at a low elevation, hardwood forest site in Michigan and compared them to similar measurements made at NWT. We hypothesized that soil emissions of  $CO_2$  and  $NO_x$  would be lower at this low elevation site due to reduced soil microbial activity associated with colder soils below a shallower and less insulating snowpack (Groffman et al., 2001). We also measured trace gases in a second plot in which the soil surface was covered with a Tedlar<sup>®</sup> sheet to investigate if the soils were the source of the trace gases in the snowpack.

## Materials and methods

## Site description

This study was conducted at the University of Michigan Biological Station (UMBS) AmeriFlux Tower site (US-UMB, 45° 33' 35.0" N, 84° 42' 49.6" W, 234 m ASL) during the snow-covered period from 24 November 2007 to 10 April 2008. The AmeriFlux Tower site is described in detail elsewhere (Schmid et al., 2003; Curtis et al., 2005; Gough et al., 2007; Nave et al., 2009). Briefly, this ecological research site is in a transition zone that is between mixed hardwood and boreal forests with bracken fern (*Pteridium aquilinum*) dominating the understory. The forest is classified as a deciduous broadleaf forest. The soil is mostly excessively drained spodosols (92.9% sand, 6.5% silt, 0.6% clay, pH 4.8) derived from glacial drift and categorized as Entic Haplorthods (Pearsall, 1995).



## Figure 1

Photos of the experimental setup (a) before and (b) after snowfall.

Each study plot was 9  $m^2$  marked off by the PVC frame. The plot in the foreground is the natural plot, where soil-snow-air interaction was allowed. The plot in the background is the Tedlar plot, where the soil-snow interaction was blocked but snow-air interaction was permitted. (c) View of the plots from the top of the AmeriFlux Tower with the Tedlar plot as the red box and the natural plot as the yellow box.

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We define winter as the period of snow cover. Leaf fall happens in early November. Snowfall typically begins in mid-November, but the site has received occasional snowfall in late October. Winter at UMBS ends the following year in April. The average winter temperature (from 1979 to 2011) at the site was -0.65°C. Maximum snow depths normally reach just below one meter (average 76 cm). Also, there is on average 270 mm of rainfall in the winter (Vande Kopple, 2011).

## Experimental setup

The gradient diffusion method (GDM) was used for inferring trace gas fluxes from chemical gradient measurements. The automated trace gas sampling system of Seok et al. (2009) was modified for use in this study. The system was expanded by a second plot to allow inferring whether the primary source of measured trace gases was biogenic (i.e., from the soil) or non-biogenic (i.e., from the atmosphere or the snowpack). Two adjacent 3 m × 3 m plots were setup 10 m east of the AmeriFlux tower prior to snowfall. Each of the two plots were marked off with a PVC-constructed frame (Fig. 1). One of the frames was wrapped in Tedlar® sheet (5 m × 5 m, 50 µm thickness; Emco Industrial Plastics, Inc., Cedar Grove, New Jersey, USA) around the bottom and the sides, leaving the top open. The Tedlar® sheet was used to prevent soil emissions and lateral flow of trace gases from the surrounding area to interact with the snowpack in the plot. A small drain was installed at one of the corners to allow snow melt and rain water to drain out of the area. The frame at the other plot was left exposed to permit soil emissions and lateral flow of trace gases into the snowpack in that area. At the center of each plot, a 1 m tall tower with multiple 30 cm long cross bars was erected. The cross bars held a pair of sampling inlets. The tower (or gradient tower) in the plot with the Tedlar® sheet (hereon labeled as the "Tedlar plot") had its cross bars positioned at 10, 20, and 30 cm above the ground in a crisscrossing pattern. Similarly, the gradient tower in the plot without the Tedlar® sheet (hereon as the "natural plot") had its cross bars placed at 2, 10, 20, 30, 40, and 90 cm above the ground also in a crisscrossing pattern. In total, there were nine paired inlets for sampling ambient and snowpack interstitial air. The purpose of having the cross bars in such arrangement was to minimize the potential artifacts caused by active sampling of snowpack interstitial air due to the close proximity of the sampling inlets to each other (Albert et al., 2002). After installing the gradient towers, snow was allowed to accumulate naturally around them in their respective plots; the snow was not disturbed in both plots throughout the snow-covered period.

The sampling line inlets were fitted with 25 mm Acrodisc<sup>®</sup> hydrophobic polytetrafluoroethylene (PTFE) syringe filters (Pall Life Sciences, Ann Arbor, Michigan, USA) to prevent debris from entering the sampling line. The sampling lines from the nine paired inlets were quarter-inch (3.9 mm inner, 6.4 mm outer) diameter PFA tubing (Parker Hannifin, Cleveland, Ohio, USA), each 10 m long, that ran from the inlets to a valve manifold, which was located in a building by the AmeriFlux tower that housed all of the instrumentation and excess tubing. The sampling lines were heated to 1°C to prevent water vapor from condensing and freezing in the lines. Air was drawn from each paired inlet for 10 min. The switching between the paired inlets was done sequentially starting from the 90 cm paired inlet down to the 2 cm paired inlet in the natural plot, and then it continued on to the 30 cm paired inlet and finished at the 10 cm paired inlet in the Tedlar plot. One cycle through all of the paired inlets took 90 min; this yielded 16 cycles per day.

Sampled air was analyzed for CO<sub>2</sub>, O<sub>3</sub>, NO, and NO<sub>x</sub> (NO + NO<sub>2</sub>) every 10 s during each 10 min sampling period. CO<sub>2</sub> was analyzed using an infrared gas analyzer (LI-7000; LI-COR, Lincoln, Nebraska, USA). The analyzer was calibrated biweekly following the procedure of Liptzin et al. (2009). A UV absorption monitor (DASIBI 1003-AH) was used to monitor O<sub>3</sub> mixing ratios. Prior to deployment of the O<sub>3</sub> monitor, it was calibrated according to the method of Brodin et al. (2010). A NO-O<sub>3</sub> chemiluminescence analyzer with a molybdenum oxide (MoO) catalyst heated to 325°C (Model 42C-TL; Thermo Electron Corporation, Franklin, Massachusetts, USA) was used to analyze for NO and NO<sub>x</sub>. NO<sub>2</sub> data were derived by subtracting the measured NO<sub>x</sub> from the measured NO data. The analyzer was calibrated biweekly using the procedure of Helmig et al. (2009). The 1003-AH and the Model 42C-TL each respectively pulled 1.8 ± 0.1 L min<sup>-1</sup> and  $1.2 \pm 0.1 L min<sup>-1</sup>$  of air through the sampling line, while the LI-7000 used the exhaust from the 1003-AH, therefore it did not require active pulling of air from the sampling line. The resulting total flow through the sampling line was  $3.0 \pm 0.2 L min<sup>-1</sup>$ .

Nitric oxide undergoes rapid oxidation through its reaction with  $O_3$ . Since the mixing ratio of NO is typically two orders of magnitude smaller than  $O_3$ , care must be taken to avoid NO losses in the sampling lines due to the gas-phase reaction with ambient  $O_3$  and to the reaction of NO during transport from the inlet to the analyzer (Helmig et al., 2009). The theoretical residence time of the trace gases in the sampling line was ~1 s. Applying the method of Helmig et al. (2009), the loss of NO was calculated to be < 3% in our sampling lines for any given moment for the  $O_3$  levels sampled in ambient air. Because  $O_3$  in the snowpack was usually < 40 nmol mol<sup>-1</sup>, losses of NO from snowpack interstitial air were expected to be lower than this estimation; consequently, we did not correct for this minor loss of NO in the sampling line.

#### Environmental parameters

Ambient air and snowpack temperatures were measured using type-E thermocouples, and soil temperature was measured using a type-K thermocouple. From the AmeriFlux tower, ambient air temperature was measured at 2 m above the ground, which is in the understory layer of the UMBS forest (Seok et al., 2013), and soil temperature was measured at 2 cm depth. In the natural plot, snowpack temperatures were measured at the 2, 10, 20, 30, and 40 cm levels on the gradient tower. Similarly, in the Tedlar plot, snowpack temperatures were measured at the 10, 20, and 30 cm levels on the gradient tower.

Snowpack depth was read daily through a webcam (LifeCam VX-1000; Microsoft Corporation, Redmond, Washington, USA) pointing to a 1 m stick ruler secured to the ground in the natural plot. Snowpack density was measured in an open area 3 m south of the natural plot. Fifteen snow pits were dug between January and April to monitor changes in snow physical properties (i.e., snow density and the formation of ice features in the snowpack). Snow properties were measured using protocols described by Williams et al. (1996; 1999).

Rain precipitation was recorded in 30 min intervals at 2 m above the ground from the AmeriFlux tower. Daily snowfall was recorded by the resident biologist at UMBS in accordance of the National Weather Service cooperative observation protocol, i.e., with a 0.093 m<sup>2</sup> (1 ft<sup>2</sup>) platform with a meter stick attached; daily snow accumulation was checked each morning at 08:00 EST. Soil moisture was measured using three water reflectometers with 30 cm long probes (CS616-L; Campbell Scientific, Logan, Utah, USA) installed vertically into the soil around the natural plot.

## Flux calculations

## Gradient diffusion flux

Trace gas fluxes through snow were calculated using a steady-state diffusion model (Fick's first law of diffusion) based on the vertical concentration gradients through the snowpack along with records of snow depth, density, and temperature following the approach of Sommerfeld et al. (1993) and as modified by Seok et al. (2009):

$$F_{\rm diff} = -\alpha D \varphi \tau \left(\frac{T}{273.15}\right)^{1.81} \frac{d\chi}{dz},\tag{1}$$

where  $F_{\text{diff}}$  is the flux of the trace gas (mol m<sup>-2</sup> s<sup>-1</sup>),  $\alpha$  is a constant for unit conversion (44.613 mol m<sup>-3</sup>), and D is the diffusion coefficient of the trace gas (m<sup>-2</sup> s<sup>-1</sup>) (see Supplementary Table S1 for values of D used for

this study).  $\varphi$  is the porosity of the snowpack calculated from the bulk density of snow,  $\tau$  is the tortuosity of the snowpack calculated from the porosity according to Du Plessis and Masliyah (1991), and T is average snow temperature (K). The mole fraction gradient (dx/dz) is the result of a difference in mixing ratio  $(dx \text{ [mol mol^{-1}]})$  between sample heights, divided by the distance (z [m]). The distance is either the distance between the inlets or the inlet and the snow surface. Snow density was surveyed 15 times throughout the season. Data gaps were filled via interpolation.

## Eddy covariance flux

Above canopy flux of  $CO_2$  was determined with the eddy covariance method (ECM). Details on the processing and analysis protocols of the turbulence data for calculating fluxes are described by Schmid et al. (2000; 2003). The fluxes were calculated in 30 min bins, yielding 48  $CO_2$  flux data points per day.

## Data processing

Snowpack-CO<sub>2</sub> data were analyzed using approaches similar to Liptzin et al. (2009). Daily CO<sub>2</sub> fluxes were calculated by averaging the 16 flux data points per day for GDM and the 48 flux data points per day for ECM. Environmental variables (snow depth, air temperature, soil temperature, and soil moisture) were tested as predictors of the daily flux using simple linear regression. The seasonal fluxes – calculated by averaging the daily fluxes – from each flux measurement technique were compared using a Mann-Whitney U-test, since the data were not normally distributed. The reactive gas data (i.e., O<sub>3</sub>, NO, and NO<sub>x</sub>) were analyzed to investigate their dependency on irradiance following Helmig et al. (2009). Data below the limit of detection (LOD) were replaced with LOD/2 for statistical analyses (Helsel 1990). All statistical analyses were conducted using MATLAB (R2012b Statistical Toolbox, The Mathworks, Inc., Natick, Massachusetts, USA) with a level of significance ( $\alpha$ ) of 0.05. Gaps in the data were due to taking the instruments offline for servicing, freezing at the sampling inlets, or damaged switching valves. Results are reported as mean ± 1 standard deviation (s.d.) unless otherwise noted.

## Results

## Snowpack and soil characteristics

Continuous snow cover over the measurement plots started on DOY 326 (22 November 2007) and ended on DOY 101 (10 April 2008) (Fig. 2). From DOY 328 to 11, the snowpack remained relatively shallow (< 40 cm). After DOY 11, the snow steadily accumulated until reaching maximum depth of 60 cm on DOY 41. Prior to the onset of snow melt (DOY 90), there were several warm (i.e., above freezing) periods, which usually were associated with rainfall, throughout the winter that led to melting at the snow surface. Subsequent freezing temperatures after these warm periods caused the formation of ice features (i.e., crusts, lenses, or layers) in the snowpack. Also, snowfall and rain events contributed to specific layering in the snowpack. The bulk density of snow increased from 180 kg m<sup>-3</sup> mid-season (DOY 11) to 380 kg m<sup>-3</sup> at the time of snow melt (DOY 95) (Fig. 2b). The average snow density during the entire season was  $240 \pm 54$  kg m<sup>-3</sup>. Soils at UMBS were relatively dry (< 15% water content), but soil moisture increased to above 25% during snow melt and above 30% during rain events.

The average temperature across depths in the snowpack ranged between -5 and 0°C, with the upper 10 cm of the snowpack occasionally cooling below -5°C, influenced by the overlying air temperature. In contrast, the soil temperature began at 4°C at the start of the measurement period (DOY 328) and steadily decreased to 1°C by the end of January (DOY 25). Afterwards, the soil temperature varied between 1 and 2°C. These recordings indicate that the soil was insulated from changing air temperature by the overlying snowpack. Air temperature varied widely with a minimum at -23°C and a maximum at 10°C before the snow melt period (DOY 90 to 101). The snowpack temperature turned isothermal during periods when air temperature was above 0°C. When the air temperature dropped below 0°C (e.g., DOY 56 to 65), a strong negative temperature gradient formed in the snowpack.

## Snowpack trace gas mixing ratios

Trace gas mixing ratios in the snowpack are shown in Fig. 3. Gaps in the  $NO_x$  and  $CO_2$  data are due to an instrument failure of the Model 42C-TL or the LI-7000, when either instrument had to be taken offline for servicing.

## Carbon dioxide

Ambient air  $CO_2$  mixing ratios ranged between 394 and 424 µmol mol<sup>-1</sup> with a median of 404 µmol mol<sup>-1</sup> during the study period.  $CO_2$  mixing ratios in the snow were noticeably different between the natural and Tedlar plots (Fig. 3a). Mixing ratios of  $CO_2$  in the natural plot snowpack were greater than in ambient air,



## Figure 2

Snowpack and soil characteristic and environmental parameters.

(a) Air temperature at 2 m. (b) Daily snow depth in the natural plot. The stars denote the locations of the ice features in the snowpack as determined during snow pit sampling at that time (right y-axis). The dashed lines indicate the levels in which the temperatures and trace gases were measured. The circles denote the bulk snow density (left y-axis). (c) Temperatures measured from the gradient tower in the natural plot. (d) Soil temperature at 2 cm depth. (e) Daily snowfall. (f) Daily rainfall. (g) Soil volumetric water content between 0 and -30 cm.

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with generally highest mole fractions closer to the soil. Also,  $CO_2$  in the snowpack rapidly increased after DOY 29, with the highest  $CO_2$  mixing ratio (1850 µmol mol<sup>-1</sup>) measured near the soil surface at the 20 cm inlets when snow height was relatively steady at 50 cm. In the Tedlar plot, the maximum  $CO_2$  mixing ratio in the snow varied between 394 and 424 µmol mol<sup>-1</sup> (406 µmol mol<sup>-1</sup> median), which was similar as observed in ambient air.

## Ozone

 $O_3$  measured from both plots yielded similar results (Fig. 3b). The mixing ratios in ambient air ranged from < 2 to 60 nmol mol<sup>-1</sup> (28 nmol mol<sup>-1</sup> mean).  $O_3$  levels increased during the study period by ~30 nmol mol<sup>-1</sup>. In both study plots,  $O_3$  mixing ratios in the snow showed similar patterns; they decreased towards the soil, with values below the instrument detection limit of 2 nmol mol<sup>-1</sup> near the soil surface.

## Nitric oxide

NO mixing ratios above the snowpack varied between < 0.10 and 1 nmol mol<sup>-1</sup>, but they were mostly below the instrument detection limit of 0.10 nmol mol<sup>-1</sup>, with the mean and median being 0.10 and < 0.10 nmol mol<sup>-1</sup>, respectively. There were no apparent differences in NO measured between the two plots (Fig. 3c), but statistical analysis indicated that snowpack-NO mixing ratios in the Tedlar plot were significantly greater than in the natural plot (p < 0.05). There were no apparent concentration gradients within the snowpack, but concentrations were on average ~0.10 nmol mol<sup>-1</sup> greater in the snowpack than in ambient air.



## Figure 3

Time series of trace gas mixing ratios in ambient air and in snow.

(a)  $CO_2$  (b)  $O_3$  (c) NO (d)  $NO_x$ The legends identified by the "snow-covered" label are data points measured in the snow at their respective inlet levels from the gradient tower.

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## Total nitrogen oxides

 $NO_x$  also showed little difference between the two plots (Fig. 3d). In ambient air  $NO_x$  varied widely between < 0.10 and 8 nmol mol<sup>-1</sup> (1.2 nmol mol<sup>-1</sup> mean). In the snow,  $NO_x$  levels generally decreased toward the soil surface as seen with  $O_3$ . The mean mixing ratio in the snow was 0.86 nmol mol<sup>-1</sup> for the natural plot and 1.1 nmol mol<sup>-1</sup> for the Tedlar plot.

## Snowpack trace gas profiles

Typical vertical snowpack trace gas profiles are presented in Fig. 4. The profiles are 20-day mean values constructed using data from DOY 52 to 72, and they are separated by study plot. These 20 days were selected because they represented the longest period with continuous measurements, had the most available data from all sampling depths, and had a relatively constant snow depth (~50 cm).

## Carbon dioxide

There was a clear gradient in snowpack- $CO_2$  mixing ratio in the natural plot with considerably higher levels seen closest to the surface. This feature was not observed in the Tedlar plot (Fig. 4a). The  $CO_2$  gradient



## Figure 4

Trace gas profiles in the snowpack by study plot.

(a)  $CO_2$  (b)  $O_3$  (c) NO (d)  $NO_2$ Data over a 20-day period (DOY 52 to 72), when snow depth was relatively stable (~50 cm), were used to calculate the mean mole fractions and the  $\pm 1$  s.d. (x-error bar) from each height in the snowpack

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indicates that  $CO_2$  was transported from the soil to the snow surface. The slope of the  $CO_2$  gradient in the natural plot was shallower (i.e., larger gradient, faster diffusion) above the 30 cm inlet height. Below the 30 cm inlet height, the gradient slope was steeper (i.e., smaller gradient, slower diffusion).

## Ozone

Both plots had similar  $O_3$  gradient profiles (Fig. 4b).  $O_3$  mixing ratios dramatically dropped by 30 nmol mol<sup>-1</sup> ~10 cm below the snow surface and continued to decrease at a slower rate towards the soil surface.

## Nitric oxide

The slopes of the NO gradients from both plots were not significantly different from zero, i.e., there were no discernible concentration gradients (p > 0.05, Fig. 4c).

#### Nitrogen dioxide

For NO<sub>2</sub>, there was a clear gradient in the snowpack (Fig. 4d) with NO<sub>2</sub> generally decreasing towards the soil surface. Between the plots, the NO<sub>2</sub> profiles were similar.

## Diurnal cycle of snowpack trace gas mixing ratios

Continuing the analysis with the 20-day dataset (DOY 52 to 72) of snowpack trace gases, we examined the relationship between solar radiation and the reactive trace gases ( $O_3$ , NO, and NO<sub>x</sub>) in the snowpack (Fig. 5). The trace gas mole fractions in the snowpack used are from the measurements at the 30 cm inlets. Snow height during this four-day period was ~50 cm, thus the 30 cm inlets were ~20 cm below the snow surface.

## Solar radiation

Solar radiation measured above the forest at 46 m above the ground had an average daily maximum intensity of  $325 \pm 228 \text{ W m}^{-2}$  (Fig. 5a).





## Figure 5

Daily cycle of solar radiation and trace gas mixing ratios in ambient air (from the 90 cm inlet) and in snow (from the 30 cm inlet).

(a) Incident radiation measured above the forest at 46 m. (b)  $O_3$ . (c) NO. (d) NO<sub>2</sub>. Data over a 20-day period (DOY 52 to 72), when snow depth was relatively stable (~50 cm), were used to calculate the diurnal averages. The shaded areas indicate the  $\pm 1$  s.d. of the mean.

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## Ozone

 $O_3$  mixing ratios in ambient air increased by 8 nmol mol<sup>-1</sup> from early morning (~03:00 EST) to late afternoon (~15:00 EST) (Fig. 5b). In the natural snowpack,  $O_3$  decreased slightly by ~1–2 nmol mol<sup>-1</sup> during the mid-day hours.

## Nitric oxide

Following the solar radiation cycle, ambient air NO increased by  $\sim$ 0.2 nmol mol<sup>-1</sup> from its nighttime minimum in the morning hours until it reached its maximum at  $\sim$ 10:00 EST. NO mixing ratios in the snowpack also increased during the day (Fig. 5c). The daily maximum of NO in the snowpack occurred three to four hours after the ambient air's daily maximum. In the natural plot, NO in the snowpack increased by 0.3 nmol mol<sup>-1</sup>, with the maximum occurring between 13:00 and 14:00 EST. In the Tedlar plot, NO in the snowpack increased by 0.4 nmol mol<sup>-1</sup>, with its daily maximum also occurring between 13:00 and 14:00 EST.



## Nitrogen dioxide

 $NO_2$  in the snow also followed the solar radiation cycle, but not as prominently as NO (Fig. 5d). In both plots,  $NO_2$  in the snow increased from a minimum at ~03:00 EST to its maximum at ~15:00 EST resembling the ambient  $O_3$  diurnal pattern. In the natural plot,  $NO_2$  increased by 0.5 nmol mol<sup>-1</sup>. In the Tedlar plot,  $NO_2$  in the snow increased by 0.8 nmol mol<sup>-1</sup>.

## Snowpack trace gas fluxes

## Carbon dioxide

In Fig. 6a, the CO<sub>2</sub> flux estimate made using ECM (above the forest at 32 m above the ground) is shown for comparison with the CO<sub>2</sub> flux determined by GDM. The CO<sub>2</sub> flux from the natural plot showed a wide spread. The highest CO<sub>2</sub> flux (1.5  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from the snow surface was observed late season (DOY 51 to 73), and prior to snowmelt, the lowest flux (0.02  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) was observed mid-winter. The seasonal average ± standard error (s.e.) was 0.54 ± 0.037  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. The spread of ECM flux was much narrower than for the GDM. The seasonal average ± s.e. estimated with ECM was 0.71 ± 0.012  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. The calculated flux was significantly higher using the ECM method (Mann-Whitney, U = 2401, p < 0.05). The upper limit of the CO<sub>2</sub> fluxes from the Tedlar plot was < 0.09  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. There was no statistically significant relationship between daily CO<sub>2</sub> fluxes estimated using ECM and GDM (Supplementary Fig. S1).

## Figure 6

Time series of trace gas fluxes through snow and seasonal averages

(a)  $CO_2$  (b) NO (c)  $NO_2$  The whisker-box plot on the right column shows the seasonal mean (square symbol) and the median (middle line in the box) flux values. The box lower and upper edges are the 25<sup>th</sup> and 75<sup>th</sup> percentiles. The 'x' symbols indicate the 1<sup>st</sup> and 99<sup>th</sup> percentiles. The '-' symbols indicate the minimum and maximum flux values. Note that the  $CO_2$  panel also has the eddy flux (ECM) results.

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## Nitric oxide

NO fluxes (Fig. 6b) were small and mostly positive. They were largest late winter between DOY 51 and 73. The fluxes ranged from -0.00014 to 0.0008 nmol m<sup>-2</sup> s<sup>-1</sup> and from -0.0003 to 0.0015 nmol m<sup>-2</sup> s<sup>-1</sup>, respectively, for the natural and Tedlar plots. The mean  $\pm$  s.e. NO flux from the natural plot (0.0003  $\pm$  0.00003 nmol m<sup>-2</sup> s<sup>-1</sup>) was less than the mean  $\pm$  s.e. flux from the Tedlar plot (0.0005  $\pm$  0.00006 nmol m<sup>-2</sup> s<sup>-1</sup>). The difference in fluxes between the plots was statistically significant (U = 1184, p = 0.00227).

#### Nitrogen dioxide

 $NO_2$  fluxes were also small but they were typically negative with large variances. The mean ± s.e.  $NO_2$  flux from the natural plot snowpack was  $-0.001 \pm 0.0002$  nmol m<sup>-2</sup> s<sup>-1</sup> and the flux from the Tedlar plot was  $-0.0003 \pm 0.0002$  nmol m<sup>-2</sup> s<sup>-1</sup>. The results between the plots were significantly different (U = 1206, p = 0.00221).

## Discussion

## Non-linearity in snowpack trace gas profiles

Snow acts as a physical barrier for diffusion of trace gases between the soil surface and the atmosphere. While the overall flux through the snowpack is driven by the concentration gradient between the source and the sink, temporal and spatial variability of the flux may be caused by specific snowpack properties (Sommerfeld et al., 1996; Winston et al., 1997; Albert and Perron, 2000), advection (Massman et al., 1997; Albert et al., 2002; Albert and Shultz, 2002; Massman and Frank, 2006; Bowling and Massman, 2011), or temporal and spatial variability in the drivers of soil biogeochemical processes. For reactive trace gases, fast chemical interactions with snow and other gases also affect the flux because these interactions can occur on timescales shorter than the transport through the snowpack. The presence of ice layers, lenses, and crusts in and on top of the snowpack can interfere with gas transport through the snowpack. The formation of ice crusts and layers in the snowpack was frequent at UMBS, due to large variations in air temperatures both above and below 0°C and rain events. This appears to be common for sites with similar weather in the winter. For instance, Schindlbacher et al. (2007) observed air temperature ranging from -19 to 12°C and rain events at their study site, which led to layering and formation of ice features in the snowpack. Schindlbacher et al. (2007) and other studies (e.g., Mast et al., 1998; Björkman et al., 2010) showed that these ice features did not seem to provide a complete barrier for trace gas transport as the gas can travel laterally around the ice features, however these features can lead to non-linearity in the profiles. It is important to consider that the rate at which trace gases are released from the soil or soil surface is not affected by properties of the snowpack; hence, the actual flux of  $CO_2$  from the soil for instance does not change, but instead, the assumptions of the diffusive model used to calculate the flux may need to be revisited.

The non-linearity observed in the  $CO_2$  profiles could be attributed to specific layering in the snowpack. It also could be caused by ventilation (Waddington et al., 1996). Albert and Hawley (2002) hypothesized that under low-wind conditions, ventilation rates are comparable to diffusion rates. Subjectively, during the measurement period, being well below the forest canopy, very calm wind conditions were experienced. Median wind speeds measured 2 m above the ground next to the natural plot, was < 0.3 m s<sup>-1</sup>. Therefore, snowpack ventilation at UMBS is less likely affecting observed gas profiles.

Albert et al. (2002) cautioned that active pulling of snowpack interstitial air can cause unwanted ventilation and interference in determining trace gas concentration in the snowpack. The sampling arms in our experiment were arranged to limit the impact of active sampling in snow following the tower setup of Seok et al. (2009) (Fig. 1). At the time of designing the snow tower, only the flow rate of the DASIBI was considered. The total flow rate in the sampling line increased when the Model 42C-TL was added. As a result, the theoretical volume (as a sphere) of air that was drawn from one inlet during the 10 min sampling time was increased to 15 L. If the seasonal bulk density of snow (240 kg m<sup>-3</sup>) is used, then the calculated effective radius will be 17 cm. It would take  $t = x^2 / 4D = (17 \text{ cm})^2 / (4^* 0.138 \text{ cm}^2 \text{ s}^{-1}) = 520 \text{ s} (or 8.7 \text{ min})$  for planar diffusion to reestablish the gradient, which is shorter than the time interval between sample collection from each inlet. Therefore, in theory, the tower arms are sufficiently separated. However, due to the presence of ice lenses and irregularities in snow density, the sampling radius will deviate from the calculated theoretical radius and the time required for the gradient to reestablish will change. The non-linearity in the  $CO_2$ concentration gradient could be attributed to not allowing for sufficient time for the gradient to reestablish after sampling from each inlet. Therefore, the observed profile below the 30 cm inlet height for  $CO_2$  (Fig. 4a) may possibly reflect the role of the deployed active sampling methodology. To work around this issue in our flux calculation, we used the top two paired inlets below the snow surface and the ambient air paired inlet to derive the concentration gradient and calculate the flux.

 $O_3$  and  $NO_2$  are soluble with Henry's constants on the order of  $10^{-2}$  (Sander, 1999), thus they are considered to be interacting gases with snow. In contrast, NO has a Henry's constant that is an order of magnitude smaller (Sander, 1999) and is, therefore, considered a gas that does not interact with snow (Bartels-Rausch et al., 2013). Since the dominating species in  $NO_x$  at UMBS was  $NO_2$ , the effective solubility of  $NO_x$  would

be similar to NO<sub>2</sub>. From past measurements (Helmig et al., 2009), we expected the O<sub>3</sub> profile in snow to resemble an exponential decay, and this was observed at UMBS (Fig. 4b). NO mixing ratios in the snow were frequently near or below the instrument detection limit, and there was a large variance in NO mixing ratios (as indicated by the error bars in Fig. 4c). This made it difficult to infer any gradient behavior in the NO profile. Our NO<sub>x</sub> profiles showed good linearity but also with large variability (Fig. 4d). The large variability was possibly due to NO<sub>2</sub> interacting with the liquid water in the snowpack and surrounding snow crystals. As NO<sub>2</sub> is transported into and through the snowpack, NO<sub>2</sub> can be adsorbed in the liquid water in the interstitial space of the snowpack and surrounding snow crystals (O'Driscoll et al., 2008). Also, the reaction with O<sub>3</sub>, NO, and other constituents in the snow would lead to flux divergence as these reactive gases can get destroyed or produced within the gradient interval. Therefore, GDM is best suited for calculating non-reactive or conserved trace gases but not for reactive gases. The flux results derived from the gradient data of these reactive gases should only be considered as a preliminary and first order of magnitude estimates of these trace gase exchanges at the snow surface.

## Sources and sinks of snowpack trace gases

Comparing the in-snow trace gas concentrations and fluxes measured from the natural plot and the Tedlar plot allows us to determine whether or not the soil, the snow, or the atmosphere act as a source or a sink to those trace gases.

#### Soil

The fact that the snowpack  $CO_2$  mole fractions in the Tedlar plot were not much different compared to ambient air  $CO_2$  levels (and that the  $CO_2$  fluxes in the Tedlar plot were nearly zero), while the snowpack- $CO_2$  mole fractions and fluxes in the natural plot were elevated (Fig. 3 and 6) provides two important pieces of information: (1) the enhanced  $CO_2$  levels observed in the snowpack are due to soil emissions, and (2) the Tedlar cover was very effective in preventing gases from the soil entering into the snowpack in this plot.

As previously noted, NO values in the snow were frequently near or below the instrument detection limit. Therefore, it was difficult to infer any gradient behavior for NO. However, as in-snow NO mole fractions from the natural plot were similar to the Tedlar plot, we concluded that microbial processes in soil (e.g., nitrification-denitrification) were not the main source of NO. Our previous studies at NWT yielded contrary results. At NWT, NO levels were largely enhanced in the snowpack, and subniveal soil NO fluxes averaged 0.05 - 0.08 nmol m<sup>-2</sup> s<sup>-1</sup> (Helmig et al., 2009). To our knowledge, there are no other NO measurements from unfertilized ecosystems in winter to compare. In non-snow covered ecosystems, temperature is thought to be an important factor controlling fluxes (Yienger and Levy, 1995). Thus, emissions should be lower in the winter than in the summer at these sites, but the causes for the two order of magnitude difference in NO fluxes between NWT and UMBS is unknown.

Soil is known to take up  $O_3$  (Turner et al., 1974; Galbally and Roy, 1980) and NO<sub>2</sub> (Stella et al., 2012; Wang et al., 2012). If the removal of  $O_3$  and NO<sub>2</sub> in snow were caused by soil uptake, then the gradient profiles of  $O_3$  and NO<sub>2</sub> in both plots would be expected to be different, with lower mixing ratios of  $O_3$  and NO<sub>2</sub> in the natural plot snowpack. However, concentrations and gradient profiles of  $O_3$  and NO<sub>2</sub> in both plots were similar. This implies that the soil or soil surface plays only a minor role in the deposition of these gases under snow covered conditions.

#### Snow

The large decrease (> 30 nmol mol<sup>-1</sup>) in O<sub>3</sub> within the first 20 cm from the snowpack surface once it enters the snowpack from the atmosphere can be attributed to the snow acting as an O<sub>3</sub> sink. This also was observed at NWT in the tundra (Bocquet et al., 2007) and subalpine meadow (Helmig et al., 2009).

The NO fluxes from the snowpack in the natural plot and the Tedlar plot are both positive (released from the snow to the atmosphere) and similar in magnitude (Fig. 6b). Since both plots have similar outward fluxes, we infer that the snowpack is the primary source of NO or serves as the medium for NO production. The NO<sub>2</sub> fluxes are bidirectional and of larger magnitude than the NO fluxes. (The bi-directionality of the NO<sub>2</sub> fluxes is discussed in a later section.) The source for NO<sub>2</sub> in the snow is likely from the photolysis of deposited atmospheric nitrate; given that the concentration levels of NO<sub>2</sub> are also higher than NO in the snow, the observed snowpack-NO is likely the secondary product of nitrate photolysis.

The currently accepted nitrate photochemistry in snow is summarized in the following reaction scheme (Frey et al. 2009).

$NO_3^- + hv \rightarrow NO_2 + O^-$	(R1)
$NO_3^- + hv \rightarrow NO_2^- + O(^3P)$	(R2)
$NO_2^- + hv \rightarrow NO + O^-$	(R3)
$NO_2^-+OH \rightarrow NO_2+OH^-$	(R4)

NO can be produced via the photolysis of nitrite  $(NO_2^{-})$  in snow (R3). It is also produced via photolysis of  $NO_2$  as follows (Boxe et al., 2005):

$$NO_2 + hv \rightarrow NO + O(^3P)$$
 (R5)

At night (in the absence of solar radiation),  $NO_2$  can hydrolyze to nitrous acid (HONO) and nitric acid (HNO<sub>3</sub>) (Chu and Anastasio, 2007).

$$2NO_2 + H_2O \rightarrow HONO + HNO_3 \tag{R6}$$

where HNO3 can undergo an autoprotolysis reaction:

$$2HNO_3 \leftrightarrow NO_2^* + NO_3^* + H_2O \tag{R7}$$

The diurnal cycle of NO<sub>x</sub> in UMBS snow was similar to that observed in the upper layers of polar snowpack, where observations by Peterson and Honrath (2001) showed that NO<sub>x</sub> concentrations increased by a factor of two to three during daytime hours. Our findings are also consistent with the three-day study conducted by (Honrath et al., 2000b) in upper Michigan, where similar diurnal dependency in NO<sub>x</sub> in snowpack air was observed. The diurnal NO cycle indicates photochemical production of NO. Likewise, NO<sub>2</sub> can also be produced via the photolysis of nitrate (NO<sub>3</sub><sup>-</sup>) (R1), as evident from the diurnal cycle seen in the data. These diurnal cycles were only observed near the snow surface in the snowpack, which indicates that this photochemistry is most active in the upper layer of the snowpack. At night, the snow can act as a reservoir for deposited NO<sub>2</sub> by "storing" it in the form of HONO, HNO<sub>3</sub> (R6), and nitrate (R7); NO<sub>x</sub> can be released back into the atmosphere during the day from the photolysis of HNO<sub>3</sub> or NO<sub>3</sub><sup>-</sup> (R1). These results illustrate that the snow acted as a source for these trace gases.

NO and NO<sub>2</sub> mole fractions in the snow during the day were ~35% higher in the Tedlar plot than in the natural plot. Given the close proximity of the two plots, it is unlikely that the two plots experienced different atmospheric deposition rates or environmental conditions that might explain this difference. A possible explanation could be that the Tedlar plot was exposed to more solar radiation than the natural plot. Although the forest – in most part – was leafless during the winter (leaf area index of 1.5 m<sup>2</sup> m<sup>-2</sup>, Seok et al., 2013), the trunks and branches attenuate solar radiation to the forest surface. A photo taken from the AmeriFlux Tower of the plots helps illustrate the conditions at the plots (Fig. 1c). Figure 1c shows similar vegetation density over both of the plots. However, the Tedlar plot (red box) has more evergreens on the south and west side than the natural plot (yellow box). Also, the AmeriFlux Tower and the building located southwest of the Tedlar plot may provide more shading for the Tedlar plot in the evening and at sunset. Unfortunately, we do not have solar radiation measurements at the plots. Therefore, we cannot further substantiate this argument. The lower O<sub>3</sub> and higher NO and NO<sub>x</sub> levels in the Tedlar plot may be a possible cause for the differences in the concentrations of these trace gases between the two plots.

The three to four-hour lag in the NO maximum in the snowpack versus the NO maximum in ambient air also can be explained by the attenuation of solar radiation by the trees. Higher solar zenith angles are required for minimal shading by the trees and for sufficient amount of solar radiation to reach the snow surface in the forest. As a result, it is during mid-afternoon hours (13:00 - 14:00 EST) that maximum photochemical reactions can occur. The cause of the morning NO maximum in ambient air is discussed in the following section.

#### Atmosphere

The gradient profile of  $O_3$  clearly shows that the source of snowpack- $O_3$  is the atmosphere. For  $CO_2$  and NO, the atmosphere is a sink as ambient air concentrations of these trace gases were lower than in-snow concentrations.

The source of nitrate and NO<sub>2</sub> in the snow is atmospheric. Extensive analyses of air mass transport at UMBS have been done using back trajectory models and correlating pollution concentration with wind direction (Cooper et al., 2001; Thornberry et al., 2001; Seok et al., 2013). Air masses from the south and southwest sectors carry higher levels of pollutants including ammonium and nitrate (Hill et al., 2005). Analyses of our data set showed that during southerly winds, NO<sub>2</sub> concentrations were higher above the snow surface than in the snow. This creates a concentration gradient with NO<sub>2</sub> transport into the snow as evident in the negative NO<sub>2</sub> fluxes (Fig. 6c). In contrast, during northerly winds, NO<sub>2</sub> concentrations were predominantly lower above the snow surface than in the snow, resulting in reversed NO<sub>2</sub> gradients with NO<sub>2</sub> release from the snow, hence the observed positive NO<sub>2</sub> fluxes (Fig. 6c).

The aforementioned trajectory studies also showed that  $NO_2$  is transported into the UMBS forest airspace during the morning hours and that a prominent NO maximum above the forest canopy occurs shortly after sunrise. Seok et al. (2013) concluded that one of the causes of the morning NO maximum (~09:00 EST) is the result of the photolysis of the advected  $NO_2$ , and that the onset of convective mixing during mid-morning is subsequently diluting the morning NO peak.



## Figure 7

Relationship between  $NO_2$  fluxes from the snow surface calculated using the gradient diffusion method and ambient  $NO_2$  above the snow surface.

The vertical dashed line indicates the compensation point (0.92 nmol mol<sup>-1</sup>), i.e., the ambient air  $NO_2$ level where the average flux shifts between emission and deposition.

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Since nitrate is considered the primary molecule for photochemical production of  $NO_x$  in the snow (Honrath et al., 2000a), the amount of nitrate required to yield the inferred  $NO_x$  flux from the surface can be estimated. With an average  $NO_2$  flux of  $10^{-3}$  nmol m<sup>-2</sup> s<sup>-1</sup>, ~0.005 kg ha<sup>-1</sup> of nitrate are converted over a 3-month period. The nitrate wet deposition data from the Douglas Lake NADP site (MI09) show a total snow nitrate content of 2.87 kg ha<sup>-1</sup>. Consequently, nitrate photolysis constitutes only a minor fraction of the deposited nitrate to be re-mobilized into the atmosphere.

## Bidirectional exchange of $NO_2$ at the snow surface

It is very interesting that the NO<sub>x</sub> flux at UMBS is bidirectional at the snow surface, unlike at NWT, where NO<sub>x</sub> was exclusively released to the atmosphere. Fluxes were negative (or NO<sub>x</sub> deposited into the snow surface) during polluted conditions, while fluxes were positive (or NO<sub>x</sub> released from the snow surface) during less polluted conditions at UMBS. This behavior is analogous to canopy-NO<sub>x</sub> exchanges tied to the effect of a compensation point, in which NO<sub>x</sub> is released from the canopy during low pollution conditions and taken up during high pollution conditions (Lerdau et al., 2000; Seok et al., 2013). The compensation point of NO<sub>x</sub> for this leaf exchange was estimated at ~1 nmol mol<sup>-1</sup> (Lerdau et al., 2000), and this value was applicable for the canopy at UMBS according to the model study by Seok et al., (2013). We analyzed the snowpack-NO<sub>x</sub> flux and ambient air NO<sub>x</sub> concentration to determine if there is a NO<sub>x</sub> compensation point for the UMBS snowpack (Fig. 7). The apparent compensation point was estimated to be 0.92 nmol mol<sup>-1</sup>. We found that 84% of the emission flux occurred during low pollution conditions (i.e., NO<sub>x</sub> < 1 nmol mol<sup>-1</sup> and winds primarily from the north and northwest sectors), and 70% of the deposition fluxes occurred during high pollution conditions (i.e., NO<sub>x</sub> > 2 nmol mol<sup>-1</sup>, with winds primarily from the south and southeast sectors).

This finding illustrates an important feature of the snowpack in forest ecosystems. It shows that the snowpack can act as a buffer or medium for regulating the reactive nitrogen cycle and reduce the effect of atmospheric deposition. Fain et al. (2013) showed that snow can effectively reduce the effect of atmospheric deposition of mercury ( $Hg_0$ ) to watersheds due to re-emission fluxes prior to snow melt. With expected snow cover decrease with climate change (Mote et al., 2005), from these connections we hypothesize that the buffering capacity of the snowpack will decline and that the dynamic range in ambient  $NO_x$  concentrations will increase, i.e., atmospheric levels will exhibit higher maxima and lower minima, and potentially alter the nutrient balance through increased leeching and runoff during rain events.

## Flux method comparison

Our analyses comparing the CO<sub>2</sub> fluxes calculated from ECM and GDM (see Supplementary Figure S1) illustrate that the two methods do not have a 1:1 relationship at daily time scales. However, ECM and GDM yielded results (ECM: 0.71  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>, GDM: 0.54  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) that differed by 24% when evaluated over the snow covered period. One explanation for this is that the changes in soil and snow properties influence the calculation and interpretation of GDM fluxes, but over a longer period, the variance in the GDM flux is averaged out. Suzuki et al. (2006) reported that their GDM fluxes were 60% smaller than ECM fluxes, and they attributed this discrepancy to difference in CO<sub>2</sub> measurement footprint size (i.e., area) and the components of the forest respiration (i.e., soil, understory vegetation, tree trunks/branches, and the canopy/ leaves). The footprint of GDM is limited to a few square meters and captures soil respiration only, while the forest. This difference in footprint and measured components of forest respiration by each method are possible explanations for the larger ECM flux values. The larger scatter in the GDM data probably is due to the multitude of variables that influence trace gas concentrations, including the physical changes of the snowpack. The impact of these changes is manifested in the non-linearity of the trace gas gradient profiles as previously discussed, which leads to a relatively larger scatter in the GDM results than in the ECM results.

Relationships between the standard environmental parameters (soil moisture, soil temperature, air temperature, and snow depth) and the daily variations in GDM and ECM fluxes of CO<sub>2</sub> were investigated by linear and polynomial regression analyses. We did not find any convincing correlation among these variables and the fluxes (Supplementary Fig. S2).

## Comparison of UMBS and NWT

For comparison, the results from this study site and the high elevation NWT study site (Soddie, 3,345 m ASL; Williams et al., 2009) are summarized in Table 1. The duration of snow cover at UMBS was 100 days shorter than at NWT. Maximum snow depth at UMBS was only 25% of the maximum snow depth observed at NWT. Average air temperature during the snow covered period was similar at -4°C for UMBS and -5°C for NWT. Although both sites had similar air temperatures, the soil at UMBS always stayed above freezing (average 1°C) even with the shallower snowpack, which provided less insulation for the soil. Climatological data show that air temperatures at NWT drop below freezing before the onset of significant snowfall in fall. In contrast, air temperatures at UMBS did not display this behavior. The difference in the timing of when air temperatures dropped and when snowfall occurred between the two sites help explain why both sites have different soil temperatures, despite both sites having similar average wintertime air temperature. Thus, the timing of the first snowfall may be more important than snow depth on the average winter soil temperature. Groffman et al. (2001) suggested that soils would become colder in a warmer climate. However, Kreyling and Henry (2011) evaluated historical trends of air, snow cover, and soil temperatures in Germany, and their findings were not able to support the theory by Groffman et al. (2001). These authors stated that the theory may only apply for high latitude and high elevation sites.

Snowpack CO<sub>2</sub> levels at UMBS did not reach as high as those measured at NWT (~1850  $\mu$ mol mol<sup>-1</sup>). Liptzin et al. (2009) ascribed deep snow (> 2 m), high productivity (annual above ground NPP of 750 g m<sup>-2</sup>), and stable soil temperatures at 0°C for the high CO<sub>2</sub> mixing ratios in snow at the soil surface. Annual NPP at UMBS is reported to be comparable to similar forest sites at ~1250 g m<sup>-2</sup> (Nave et al., 2009). When fine root and below ground NPP are excluded, above ground NPP at UMBS yields ~615 g m<sup>-2</sup> (Nave et al., 2009). Thus, the above ground productivity is less than at NWT, but the difference in NPP is not enough to result in an order of magnitude lower maximum CO<sub>2</sub> concentration in snow.

The deep snow at NWT creates a stable soil environment allowing for the evolution of a phylogenetically and physiologically unique community of microbes to thrive in the winter soils as cold as  $-5^{\circ}$ C (Brooks et al., 1996; Schadt et al., 2003; Brooks et al., 2005; Monson et al., 2006b; Schmidt et al., 2008). In certain regions of the NWT domain, the soils were covered by "snow molds" (Schadt et al., 2003; Schmidt et al., 2008). These "snow molds" were found to have high metabolism and growth rates in cold temperatures under snow, and they are thought to contribute to the temperature-sensitive, high CO<sub>2</sub> fluxes under snow observed at NWT (Monson et al., 2006b; Schmidt et al., 2008). We are not aware of any wintertime soil microbial studies at UMBS to conclude that the lower CO<sub>2</sub> fluxes at UMBS (compared to NWT) could be linked to differences in or lower abundance of microbes in the soil.

CO<sub>2</sub> flux through snow at UMBS (0.52  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) was higher than reported estimates of CO<sub>2</sub> flux through snow at other deciduous forest sites that range from 0.22–0.37  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Mariko et al., 2000; Mo et al., 2005; Suzuki et al., 2006) and was more comparable to the NWT CO<sub>2</sub> flux of 0.71–0.86  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Liptzin et al., 2009) and those found for evergreen forests of 0.32–0.84  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Sommerfeld et al., 1993; Sommerfeld et al., 1996; Mast et al., 1998; Hubbard et al., 2005). Despite the relatively high wintertime CO<sub>2</sub> flux, this constitutes only ~5% of the annual respiration at UMBS (1450 g-C m<sup>-2</sup>). This is similar to reported values of 7-10% at other deciduous forest sites (Mariko et al., 1994; Mo et al., 2005), and less than the NWT result of 30% (Liptzin et al., 2009).

Table 1. Comparison of the U	<b>Jniversity of Michigan</b>	<b>Biological Station</b>	(UMBS) results and	d the Niwot Ridge,	Colorado
(NWT) Soddie site results		-		-	

	UMBS		NWT (Soddie)				
Soil and snow characteristics	Natural plot	Tedlar plot	Natural plot				
Snow cover duration (days)	140	140	220ª				
Maximum snow depth (cm)	60	60	220ª				
Snow density (kg m <sup>-3</sup> )	180-380	180-380	200-500 <sup>b</sup>				
Mean ambient air temperature (°C)	-4	-4	-5ª				
Mean soil temperature (°C)	1	N/A	0ª				
Mean soil moisture (%)	16	N/A	35ª				
Soil C:N ratio	28°	N/A	12 <sup>d</sup>				
Above ground NPP (g m <sup>-2</sup> )	615°	N/A	750ª				
Snow nitrate conc. (µM)	28 <sup>f</sup>	28 <sup>f</sup>	11 <sup>g</sup>				
Trace gas mixing ratios (mean, min-max)			·				
Above snow							
CO <sub>2</sub> (µmol mol <sup>-1</sup> )	405, 394–424	405, 394–424	386 <sup>b</sup>				
O <sub>3</sub> (nmol mol <sup>-1</sup> )	28, < 2-60	28, < 2-60	42 <sup>h</sup>				
NO (nmol mol <sup>-1</sup> )	0.10, < 0.1-1	0.10, < 0.1-1	< 0.1-1 <sup>h</sup>				
NO <sub>x</sub> (nmol mol <sup>-1</sup> )	1.2, < 0.1-8	1.2, < 0.1-8	0.5–6 <sup>h</sup>				
In snow							
CO <sub>2</sub> (µmol mol <sup>-1</sup> )	Max 1850	Max 424	2006: Max 8400ª 2007: Max 10000ª,b				
O <sub>3</sub> (nmol mol <sup>-1</sup> )	10, < 2-42	11, < 2-53	< 1-40 <sup>h</sup>				
NO (nmol mol <sup>-1</sup> )	0.2, < 0.1-1	0.23, < 0.1-1.6	< 0.1–14 <sup>h</sup>				
NO <sub>x</sub> (nmol mol <sup>-1</sup> )	0.86, < 0.1-5	1.1, < 0.1-5.5	< 0.1-4 <sup>h</sup>				
Trace gas fluxes through snow (mean, min-max)							
CO <sub>2</sub> (µmol m <sup>-2</sup> s <sup>-1</sup> )	GDM: 0.54, 0.02–1.5	0.02, 0-0.09	2006: 0.71, 0.66-1.09 <sup>a</sup>				
	ECM: 0.71, 0.39–1.3*		2007: 0.86, 0.58-1.08ª				
NO (× 10 <sup>-3</sup> nmol m <sup>-2</sup> s <sup>-1</sup> )	0.3,-0.14-0.8	0.5, -0.3 -1.5	N/R				
$NO_x (\times 10^{-3} \text{ nmol m}^{-2} \text{ s}^{-1})$	-0.9, -9-2.6	-0.3, -6-1.6	5-8 <sup>h</sup>				

N/A, not applicable; N/R, not reported

<sup>a</sup>Liptzin et al. (2009)

<sup>b</sup>Seok et al. (2009)

Derived by subtracting the total NPP with belowground and fine root NPP (Nave et al., 2009)

<sup>f</sup>Assuming no loss or gain from internal transformation or from dry deposition. National Atmospheric Deposition Program data (MI09 site for winter 2007)

<sup>g</sup>Williams et al. (2009a)

<sup>h</sup>Helmig et al. (2009)

\*Above snow flux determined using the Eddy covar. method

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The NO emissions might differ between UMBS and NWT because of differences in N cycling. At NWT, nitrate is present in the soil solution throughout the summer, suggesting that nitrification must be occurring (Williams et al., 2009). While nitrate measurements were not available at UMBS, the forest floor C:N ratio is 28 (Nave et al., 2011). Studies from both Colorado (Rueth and Baron, 2002) and Europe (Gundersen et al., 1998) suggest that N mineralization produces excess nitrate below a C:N ratio of ~30. Thus, it may be that the UMBS site is still N-limited enough such that nitrate is relatively low for NO to be produced from N-cycling processes.

## Conclusions

A warming climate will affect snow cover in multiple ways. It will potentially cause a later onset of winter snow cover, an overall shallower snowpack, and earlier springtime snow melt. There may be more wet snow from warmer winter temperatures. Furthermore, currently snow-covered lower elevation sites will possibly become snow-free ("at risk snow"). All of these changes will impact wintertime soil trace gas fluxes. The

<sup>&</sup>lt;sup>c</sup>Nave (2011) <sup>d</sup>Hood et al. (2003)

timing of the onset of the winter snowpack is likely of particular importance – as shallower snowpack will decrease the insulation effect – that will potentially allow soils to become colder during mid-winter, which would suppress winter soil biogeochemical processes. Our data did not support the hypothesis that soil emission of  $CO_2$  and  $NO_x$  would be lower at UMBS due to reduced soil microbial activity associated with colder soils below a shallower and less insulating snowpack. Instead, we observed warmer soils and  $CO_2$  fluxes in the same order of magnitude as at NWT. However, wintertime  $CO_2$  emissions were likely less important in determining the annual C budget at the site, as these constituted only ~5% of the annual C budget.

From our Tedlar plot measurements, we validated that the soil was the source for  $CO_2$ . We also concluded that the snow was a sink for  $O_3$  and a medium for bi-directional exchange of  $NO_x$  with the atmosphere, similar to forest canopy  $NO_x$  exchange. There are two implications of these results. One is that the snowpack acts as a buffer or medium for regulating the reactive nitrogen cycle in forest ecosystems. We hypothesize that as snow cover decreases with climate change, the buffering capacity of the snowpack will decline and the dynamic range in ambient  $NO_x$  concentrations over (currently) snow-covered regions will increase, i.e., atmospheric levels will exhibit higher maxima and lower minima, and alter the nutrient balance through increased leaching and runoff during rain events. Another implication of the result is that the interaction that the snowpack has with its overlying atmosphere is not globally uniform. Hence, caution should be taken when extrapolating results to other snow-covered environments and implementing wintertime biogeochemical processes observed at one site to other sites in model studies.

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## Contributions

- Contribution to conception and design: BS, DH, MWW, CSV
- Contribution to acquisition of data: BS, CSV
- · Contribution to analysis and interpretation of data: BS, DH, DL, MWW
- Drafted and/or revised the article: BS, DH, DL, MWW
- · Approved the submitted version for publication: BS, DH, DL, MWW, CSV

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## Competing interests

The authors have declared that no competing interests exist.

#### Supplementary material

- Table S1. Diffusion coefficients  $D^a$  of trace gases used in the gradient diffusion method.
- Figure S1. Comparing daily CO<sub>2</sub> flux values calculated using two different methods. Scatter plot of flux calculated using the eddy covariance method (ECM) versus the gradient diffusion method (GDM) color coded by snow cover periods: early winter (black, DOY 328 to 8), mid-winter (red, DOY 9 to 54), late winter (green, DOY 55 to 94), and snowmelt (blue, DOY 85 to 101).
- Figure S2. Environmental predictors of daily CO<sub>2</sub> fluxes. Fluxes estimated using the gradient diffusion method (GDM) are in squares and using the eddy covariance method (ECM) are in triangles. The solid line is the linear regression fit for GDM; the dashed line is the fit for ECM. Their corresponding slope (s) and R<sup>2</sup> values are labeled by their regression line. The text in the red denotes that the slope was not significantly different from zero at the 0.05 level. The snow covered season was divided into early (black, DOY 328 to 8), mid (red, DOY 9 to 54), late (green, DOY 55 to 94), and melt (blue, DOY 85 to 101) periods.

#### Data accessibility statement

Data will be available on the UMBS Data Management Website (http://umbs.lsa.umich.edu/research/data-management) and made accessible in accordance to the policy described by the UMBS Data Management Policy (http://umbs. lsa.umich.edu/research/datapolicy).

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