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Diffusional flux of CO_2 through snow: Spatial and temporal variability among alpine-subalpine sites

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Abstract. Three alpine and three subalpine sites were monitored for up to 4 years to acquire data on the temporal and spatial variability of CO_2 flux through snowpacks. We conclude that the snow formed a passive cap which controlled the concentration of CO_2 at the snow-soil interface, while the flux of CO_2 into the atmosphere was controlled by CO_2 production in the soil. Seasonal variability in the flux at all sites was characterized by early winter minima followed by a rise in flux that averaged 70% above the minima over about a 1-month period. The seasonal variability was not related to soil temperatures which remained relatively constant. Interannual variability was small, and spatial variability was smaller than previously reported. Spatial variability on a scale of 1 to 10 m was less than 30% of the average fluxes and not significantly greater than estimated error in most cases. Spatial variability on a scale of 10- to 100-m was about a factor of 2 and on a scale of 100 to 1000 m was about a factor of 4. The 100- to 1000-m variability was complicated by the fact that the sites were in different ecosystems, alpine and subalpine, and at different elevations. We attribute the small variability at the 1- to 10-m scale to the deep snow cover, from 1.4 to 5 m. We hypothesize that horizontal diffusion under the snow cover reduced small-scale horizontal gradients, while the insulating effect of the deep snow cover kept the soil temperature and moisture relatively constant. Equivalent annual wintertime flux averaged about 95 g C m^{-2} yr^{-1} in the alpine and about 232 g C m^{-2} yr^{-1} in the subalpine sites. Measurements of CO_2 concentrations at 0.2 and 0.5 m in the soil of one of the subalpine sites indicated that production early in the snow season occurred at or below 0.5 m while production between 0.5 m, and the surface became important after the start of the melt season.

Introduction

The flux of CO_2 through snow covers may constitute an important part of the carbon balance in alpine and subalpine ecosystems [*Sommerfeld et al.*, 1993]. Snow may cover between 44 and 53% of the land area of the northern hemisphere during the winter [*Barry*, 1992]. In high elevation and high latitude areas the soil may be snow covered for the greater part of the year. The insulating effect of deeper snow covers can allow the underlying soil to maintain temperatures above -6.5°C, which is thought to be the lowest temperature at which CO_2 production occurs [*Coxson and Parkinson*, 1987]. CO_2 production in soils varies in time and space, and this variation is reflected in variations in the fluxes through snow. It is important to characterize this spatial and temporal variability both to evaluate the importance of subnivian CO_2 production on the global carbon budget and to help understand the controls on CO_2 production under snow. We have measured the fluxes of CO_2 through snowpacks at alpine and subalpine sites in the Glacier Lakes Ecosystem Experiments Site (GLEES) in south central Wyoming for four seasons. The results should provide a basis against which other measurements can be compared. *Musselman* [1994] gives a comprehensive description of the GLEES.

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Sites for Sample Locations

To investigate the spatial variability of CO_2 flux, six sites at separations between about 50 and 2000 m were established. Three of the sites were representative of the local alpine ecosystem, and three were representative of the local subalpine ecosystem. In selecting the sites, we attempted to maximize the differences in CO_2 production by choosing sites with different vegetation, soil development, and wetness. To evaluate temporal variability, one alpine and one subalpine site were maintained for more than 3 years. Four additional sites were sampled for one snow season each; two in 1992-1993 and two in 1993-1994. At five of the sites we established pairs of sampling

locations separated by 2 to 4 m. At the sixth (subalpine) site we used four of the sampling locations described by *Mosier et al.* [1994], which were separated by 5 m each and included sample tubes at 0.2 and 0.5 m in the soil. This site was sampled in 1992-1993

Alpine Sites

The alpine sites are located at the alpine and subalpine ecotone at the GLEES. The main alpine site at about 3290 m above sea level (HILL) was maintained for 3 years, April 1991 through June 1993. The site is a dry, wind-exposed ridge between East and West Glacier Lakes and the environment here is harsh. The wind averages 11 m s^{-1} in the winter and 5 m s^{-1} in the summer. The vegetation is primarily grasses and cushion plants; although there are a few small, scattered, *Picea engelmannii*, *Abies lasiocarpa*, *Juniperus communis* variety *depressa*, and *Salix brachycarpa* near the site. Ground cover species found here include *Vaccinium scoparium*, *Festuca brachyphylla*, and *Selaginella densa*. Vegetative cover is sparse. Soils are thin and rocky with very little soil development. The maximum snowpack here averages 1.8 m, about 90% of the average for GLEES [*Musselman*, 1994], and the well-drained soil dries soon after snowmelt. This site is the highest in elevation and therefore has a lower average air temperature with the snowmelt beginning later in the season than average for GLEES. This site was chosen because it was expected to have a relatively low CO_2 flux. The two sample locations at this site were separated by about 4 m.

The second alpine site, West Glacier Lake (WGL), at the elevation of the HILL site and about 400 m to the southwest was sampled from late December 1993 through April 1994. It is a large alpine meadow, fed by snowmelt early in the season, but typically becoming dry in July or August. It is protected from the prevailing wind direction by topography and nearby trees. There is a considerable amount of exposed rock. Primary cover species are *Geum rossii* and *Sibbaldia procumbens*. *Artennaria umbrinella*, *Potentilla diversifolia*, *Danthonia intermedi*, *Juncus drummondii*, *Vaccinium scoparium* and *Carex rossii* also occur on the site. The two sample locations at this site were separated by about 3 m and were sampled for one snow season in 1993-1994.

The third alpine site, a wet alpine meadow (WAM) located about 200 m northeast of the HILL site in a small gully, was sampled from November 1992 through June 1993. An ephemeral stream runs through the gully in the spring and early summer, fed by a large, uphill snowpack. The gully also accumulates the deepest snowpack of all the sites; 5 m during the sampling year. The area is vegetated primarily with *Deschampsia cespitosa*, *Carex nigricans*, and *Caltha leptosepala*, with smaller amounts of *Carex aquatilis* and *Juncus drummondii* present. The site is somewhat sheltered from the prevailing winds and is surrounded by sparse forest near timberline. Soil is thicker than the nearby HILL site. Vegetation is also denser, because of the protection and wetter conditions than the HILL site. This site was sampled for one snow season in 1992-1993 at two sample locations separated by about 4 m.

Subalpine Sites

The main subalpine site (BRK) was maintained for 4 years, April 1991 through May 1994. It was chosen to contrast with the main alpine (HILL) site. The BRK site is a small meadow, about 25 m in diameter, surrounded by forest except for a small opening leading to a larger open area about 20 m to the southwest. The surrounding forest protects the location from prevailing winds. Wind below the canopy top averages about 3 m s^{-1} in winter and about 2 m s^{-1} in the summer. The common species are *Deschampsia cepitosa* and *Caltha leptosepala*. Soils are shallow, rocky, and dry after snowmelt. The environment is much less harsh than the alpine site. The soil appears to hold its moisture longer, and being at lower elevation (3180 m), it is warmer. This site was chosen with the expectation that the CO_2 flux would be higher than at the alpine sites. The two sample locations at this site were about 10 m east of the forest edge and were separated by about 3 m.

The second subalpine site (FOR) is about 100 m west of BRK in a dense *Picea engelmannii* forest stand, with almost no understory vegetation present at the site, but *Vaccinium scoparium* occurs in the immediate area. There is a thick layer of fine woody debris and duff from twigs and needles from the overstory trees. The snowpack here is the thinnest and spatially the most variable in depth. This site was sampled for one season, September 1993 through April 1994 at locations separated by about 2 m.

Locations M3, M4, M5, and M6 (3 to 6 in the work of *Mosier et al.* [1993]) were 130 (M6) to 145 m (M3) west of BRK. They are in a wet meadow about 20 m wide by 70 m long, along a relatively flat drainage basin, with a ephemeral stream channel which flows during snowmelt but, the stream dries after snowmelt is complete, generally in early July to early August. M3 and M4 grade from the drier *Picea engelmannii* forest toward the wetter center of the meadow. Common species here are *Deschampsia cepitosa* and *Caltha leptosepala*. *Salix planifolia* occurs frequently on the east edge (M3) of the meadow. The center of the meadow (M5 and M6) is wet, with characteristic species being *Erigeron ursinus* and *Plantago tweedyi*. Also present are *Trisetum spicatum* and *Achillea millefolium*. The four sample locations were each separated by about 5 m each, starting about 3 m east of the forest edge. Sampling was conducted from December 1992 through May 1993. This site was chosen with the expectation that it would have the highest CO_2 fluxes.

Methods

At each site, gas collectors [*Sommerfeld et al.*, 1991] were installed at the soil surface before accumulation of the seasonal snowpack. Access tubing was taped to a 3-m-long piece of 1/2 inch (13 mm) metal tubing set vertically more than 1 m from the sample location to allow sampling without disturbing the snow directly over the sample location. After the winter's snow cover began to accumulate, samples were drawn from the collectors and from the ambient atmosphere on a variable schedule. The snow depth at the time of sampling was measured by the height of the metal tubing above the snow surface at each location. The samples were analyzed by gas chromatography. The diffusional

fluxes through the snow covers were estimated by two different methods. When snow stratigraphy data were available from snow pits dug within 1 day of the sample, the model of *Massman et al.* [1995] was used. This was the more accurate technique because the model accounts for layer porosity, tortuosity, and thickness. At other times a volume-weighted mean porosity and total snow thickness were used. The volume-weighted mean porosities were estimated from interpolations of snow pit data.

Gas Analysis

Gas collector installations at the base of the snowpacks were as described by *Sommerfeld et al.* [1991]. Soil gas collectors at M3 through M6 were sections of 1/8 inch (3 mm) stainless tubing embedded in epoxy in 1 inch (25 mm) polyvinyl chloride (PVC) tubing. Each section of stainless tubing pierced the wall of the PVC tubing at a sampling level from 0.1 to 0.5 m. The ends of the stainless sections were finished flush with the outside surface of the PVC tubing at each level. The other ends protruded above the soil surface when these probes were forced into close fitting holes cored in the soil. The levels 0.2 and 0.5 m in the soil were sampled for one season in 1992-1993.

Twenty-mL nylon syringes were used to draw the gas samples and transport them to a Hewlett Packard 9730 gas chromatograph with a 3 M Haysep D column and a thermal conductivity detector. Samples were analyzed within 4 hours of collection. Tests showed that samples of 2000 parts per million by volume (ppmv) stored in the syringes decreased in concentration by about 5% in 24 hours.

In 1991, standard gases of approximately 350 and 2000 ppmv from Air Products, Inc. were used as working standards for the analyses. Starting in 1992, the 350 ppmv working standard was calibrated against a primary standard tank of 343.2 ± 0.4 ppmv obtained from the National Institute of Standards and Technology. In addition, higher-concentration working standards of approximately 1000, 2000, and 4000 ppmv were calibrated against a mixture of 99.99% CO_2 (Air Products Inc.) and dry artificial air. Mixing was done using mass flow meters calibrated against a Hastings model HBM-1A bubble flow meter, which has an accuracy of better than 1%. The precision of these calibrations, as estimated from the scatter in the results, was better than 1%. On occasion, the precision of the gas chomatograph was no better than 2% as estimated from scatter in the calibrations using the working standards. Therefore we conservatively estimate the accuracy of the calibration measurements as ± 2% in the range 300 to 4000 ppmv.

The calibrations allowed determination of the calibration constant (ppmv/signal curve area) for the range 0 to 4000 ppmv. This calibration and subsequent operation showed that the gas chromatograph had a small, nonlinear response in the range 0 to 2000 ppmv, which varied from run to run. A linear extrapolation from 0 through 350 ppmv could result in an error at and above 4000 ppmv of up to 5%. This result was unexpected since this type of instrument is usually assumed to be linear within about 2% over its entire range. To compensate for this behavior between 0 and 2500 ppmv, we fitted a polynomial to the working gas calibrations for each day and used that calibration curve to correct the gas analyses. For the range 0 to 2500 ppmv, accuracy is about 2%, the estimate of the calibration accuracy. When the 4000 ppmv tank was exhausted, we concentrated our calibration efforts in the range 0 to 2000 ppmv where the gas chromatograph exhibited nonlinearities larger than 2%. This was justified by the many comparisons between the 2000 and 4000 ppmv tanks which were linear within 2%. We assumed from the calibration data between 2000 and 4000 ppmv that extrapolation from 4000 to 10,000 ppmv could be done with sufficient accuracy for our purposes. This assumption is required to recover data greater than 4000 ppmv. Data in this range (about 14% of the total) were initially unexpected. Because of the extrapolation, the accuracy of the concentrations above about 2500 ppmv is conservatively estimated to be 5%, and for simplicity in the following we have taken a conservative estimate of the accuracy of all measurements as 5%. There are three measurements (about 1% of the total) above 6000 ppmv, but since the nonlinearity of the measurements decreased with concentration, we believe their accuracy is also within our estimate. As discussed below, the errors involved in estimating the porosities of the snow covers for the flux calculations are greater than 5%, so the errors of these analyses are small compared to other errors.

Snowpack Properties

The most important snow properties for the estimation of diffusional flux are the porosity profiles and the layer thicknesses [*Massman et al.*, 1995]. Snow pits were dug at times throughout each winter to determine the porosity profiles from measurements of densities and stratigraphy using standard snow pit techniques. Pits were dug as close as practical to the sampling sites but not so close as to affect the gas flux at the sampling sites. All sites except FOR had snowpacks which were relatively flat and uniform. Therefore the stratigraphy of the sampling sites was assumed to be the same as that determined from the snow pits, with individual layers linearly scaled for differences in snow depth. This assumption may not have been accurate for the FOR site. Snow pits were backfilled after stratigraphy determinations. For sampling times that did not correspond closely to the snow pit times, we used a time-weighted average of the volume-weighted mean porosities of the snow pits before and after the sampling dates.

Experience has shown that if the layering is properly identified, scatter in density (porosity) measurements within each layer is about 10%. Since this scatter is random, inaccuracies in the averages are expected to decrease by n^{-2}, where n is the number of layers, usually about 10. However, the snow pits were dug a few meters from the gas measurement sites and often porosities were estimated from the porosities of the two snow pits closest in time. We therefore concluded that unless the layers were more than 20 cm thick, taking more than one sample per layer would not materially increase the accuracy of the porosity estimates. We make a conservative estimate of the accuracy of the volume-weighted mean porosity estimates as 10%. The error estimate must remain somewhat subjective based on experience. An objective estimate of the error would have involved destroying the sample site.

Ice lenses were rare. Only single layers were observed in pits dug after the middle of April, and they disappeared in about 2 weeks. Their porosity is difficult to characterize. However, they

Table 1. Comparison of Fluxes Estimated by a Layer Model and a Volume-Weighted-Mean Porosity Model for Days on Which Snow Pit Information Was Available

Site	Layer Model Average, mg m^{-2} s^{-1} CO_2	VWM Model Average	Mean Differences	Standard Deviation of Differences
HILL-A	0.0143	0.0149	0.0005	0.0004
HILL-B	0.0114	0.0123	0.0008	0.0012
WAM-A	0.0178	0.0188	0.0009	0.0001
WAM-B	0.0168	0.0176	0.0008	0.0002
BRK-A	0.0255	0.0266	0.0011	0.0002
BRK-B	0.0250	0.0261	0.0011	0.0004

are very thin compared to the total snow thickness, so that large errors in estimating their porosities add only a small error to the volume-weighted porosities. The influence of an ice layer would only be dramatic if its porosity were 0, but such ice layers are never observed in this region. That such layers do not exist is shown by the concentration profiles reported by *Sommerfeld et al.* [1993], *Mast et al.* (1994), *Massman, et al.* (1995), and unpublished profiles obtained during the course of this study. These profiles were basically linear and thus showed no evidence for any significant impermeable layer.

Flux Calculations

Assuming one dimensional flux, the diffusional flux follows Fick's law

$$J = -\phi \tau D \left(\frac{dc}{dz}\right)$$

where ϕ is the porosity of the layer, τ is the tortuosity of the layer, D is the diffusion coefficient for CO_2 in air and dc/dz is the concentration gradient across a uniform layer. We assumed that $\tau = 1$. Tortuosity is a difficult quantity to measure and proved impossible for the number of samples taken. Nevertheless, limited measurements of the tortuosities of snow layers near sites M3-M6 indicate a value between 0.75 and 0.9 (W. Massman et al., manuscript in preparation, 1996) suggesting that we may have overestimated our flux by 10 to 25%.

Wind pumping may also affect the flux [*Albert and Hardy*, 1995; *Massman et al.*, 1995; W. Massman et al. manuscript in preparation, 1996] However, the magnitude of the effect is still unclear.

The snow depth and the diffusion coefficient of CO_2 in air are known to better than 1%. Thus, apart from tortuosity and possible wind effects, most of the error resides in estimates of concentration (5%) and porosity (10%). A conservative estimate of the accuracy of the product of porosity and concentration is then 11% [*Goodman*, 1960] which we take as the accuracy of the flux estimates. Again, the estimates at the FOR site may not be this accurate because of variable snow depth. If our estimate of the accuracy of the of the concentration measurements is degraded to 10%, the overall error would be 14% [*Goodman*, 1960].

Results

Stratigraphy Model Comparisons

Before flux data from individual sites were evaluated, it was necessary to determine and correct any inaccuracy involved in using volume-weighted mean porosities when snow pit data were not available. A comparison between the fluxes calculated using the layer model and fluxes calculated using volume-weighted mean porosities from 28 sets of concentration data is shown in Table 1. Errors created by using the volume-weighted mean porosities are up to about +5% and averaged +4.4% of the flux for all the measurements. On the basis of our results, diffusional fluxes calculated for time periods without snow pit data were reduced by 4.4%. This correction was also applied in determining average fluxes presented in Table 2.

Alpine Sites

HILL. Data for the HILL site include measurements from April 1991 through June 1993. The average fluxes for the period studied are shown in Table 2. The two locations differ by about 6% of the average flux, not a significant difference given an error estimate of 11%. The standard deviation of the daily differences is about 30% of the flux indicating short-time variations in the fluxes. The seasonal temporal variability is consistent from year to year. Each year exhibits a minimum early in the calendar year, a rise to a maximum which begins at about the time of onset snow melt, and a drop before the snow disappears (Figure 1a). The rise averaged about 95% over the minima with a duration of about 1 month.

WAM. For this study, the lowest data point (WAM A, May 25, 1993) was removed from the data set. At the time that measurement was made, water was observed to be running beneath the snow cover. In a few days a large hole opened in this snow cover and the concentrations at this sampling location dropped to about 2000 ppmv. Because of the water flow, we think this point is more representative of the concentration upstream of this sampling location. Temporal variability is similar at the two sample locations both of which exhibit the early winter minima and a rise to a maximum averaging 70% higher over a 1 month period, corresponding approximately to the onset of melting. This site has an average flux intermediate between the other alpine sites and the subalpine sites (below). The averages differ by about 10%, and the standard deviation of the daily differences is about 15% of the average flux. Both are

Table 2. Summary of CO_2 Fluxes

Location	Number of Samples	Average, mg $m^{-2} s^{-1}$ CO_2	Standard Deviation	Coefficient of Variation	Maximum	Minimum	Range	S. D. of Daily Differences
Hill A	25	0.0097	0.0043	0.44	0.0224	0.0040	0.0184	0.0032
Hill B	25	0.0103	0.0046	0.35	0.0238	0.0042	0.0196	
WGL 2	7	0.0088	0.0024	0.30	0.0112	0.0054	0.0057	0.0012
WGL 4	5	0.0071	0.0026	0.37	0.0096	0.0044	0.0052	
WAM A	12	0.0136	0.0051	0.37	0.0265	0.0038	0.0228	0.0058
WAM B	10	0.0167	0.0062	0.37	0.0304	0.0115	0.0189	
BRK A	30	0.0189	0.0050	0.27	0.0330	0.0083	0.0247	0.0040
BRK B	30	0.0184	0.0035	0.19	0.0253	0.0071	0.0182	
FOR A	9	0.0140	0.0090	0.65	0.0363	0.0064	0.0300	0.0151
FOR B	7	0.0229	0.0084	0.37	0.0384	0.0156	0.0228	
M3	11	0.0372	0.0062	0.17	0.0484	0.0283	0.0200	0.0043
M4	8	0.0369	0.0076	0.21	0.0480	0.0233	0.0247	
M5	11	0.0320	0.0080	0.25	0.0476	0.0215	0.0261	0.0034
M6	11	0.0359	0.0055	0.15	0.0456	0.0300	0.0156	

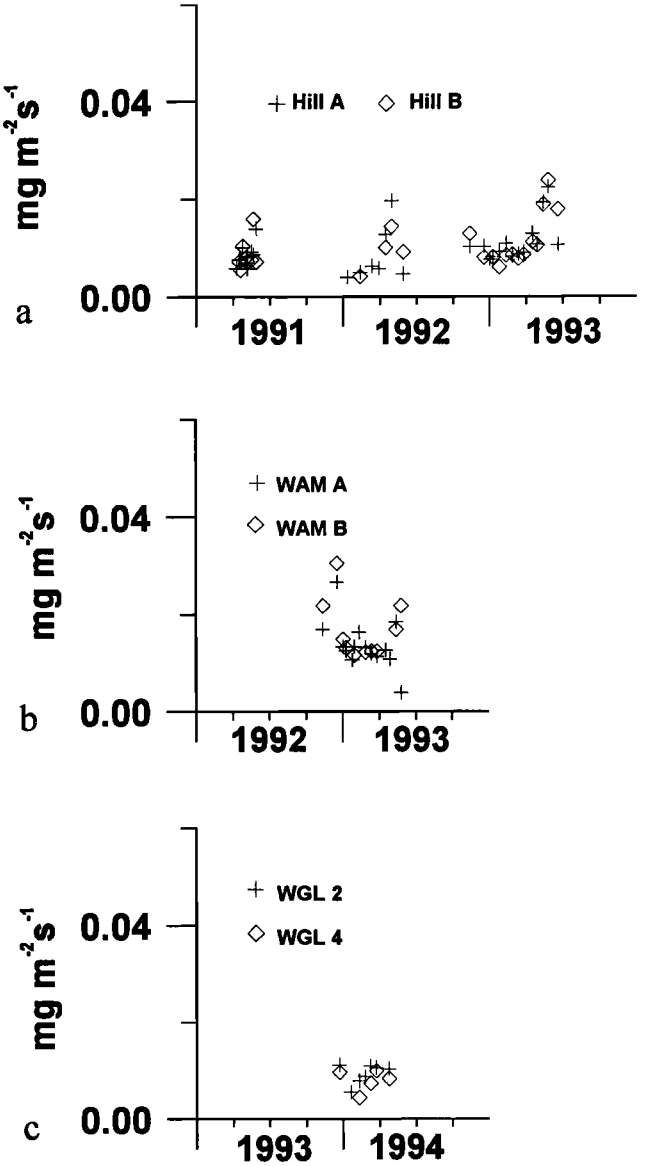

Figure 1. Time series of CO_2 at the different sites: (a) HILL, (b) WAM, (c) WGL, (d) BRK, (e)FOR, and (f) M3 - M6.

close to the estimated error of 11%, indicating no seasonal or short-time difference between locations. This site had the thickest snowpack, which should have been the most effective in decreasing horizontal gradients.

WGL. This site had average fluxes about 20% smaller than the HILL site and with a smaller range. Temporal variability is similar between the two sample locations and to the HILL site, with the early winter minimum rising to an average 80% higher over a 1-month period. In this case the rise started well before the melt period (Figure 1c). The averages differ by about 15%, and the standard deviation of the daily differences is about 16%, only slightly higher than the estimated error. Thus the seasonal and short-term differences may not have been significant.

Subalpine Sites

BRK. The most extensive data are available from the BRK site (Figure 1d). The 1991 data collection began in the beginning of April and continued to the end of March 1994. In 1992-1994, minima in the fluxes were observed in the first quarter of each year, and maxima were observed in April at approximately the time that melt starts. In 1991-1993 the maxima are followed by a distinct drop in flux just before the snow disappears. The maxima averaged about 25% higher than the minima and rose over about a 1-month period. Ranges and averages of the fluxes are in close agreement for the 4 years. The averages differ by about 10% , not higher than the estimated error. The standard deviation of the daily differences between the locations at this site is about 20% of the average flux, indicating some short-time variability between the fluxes.

FOR. This site showed the greatest range of fluxes but also had the early winter minima rising to maxima averaging 60% higher in about 2 weeks. The rise started before the onset of melting and persisted about 1 month. Drifting and to a smaller extent interception caused uneven snow deposition which made it difficult to estimate the effective snow depth at each location. The average flux was about the same as BRK. The averages differed by about 20%, and the standard deviation of the daily differences was about 80% of the average flux, both significantly larger than the estimated error. However, because the estimated error in the porosity and depth may not be reliable at this site, the 20% difference between averages may not be significant.

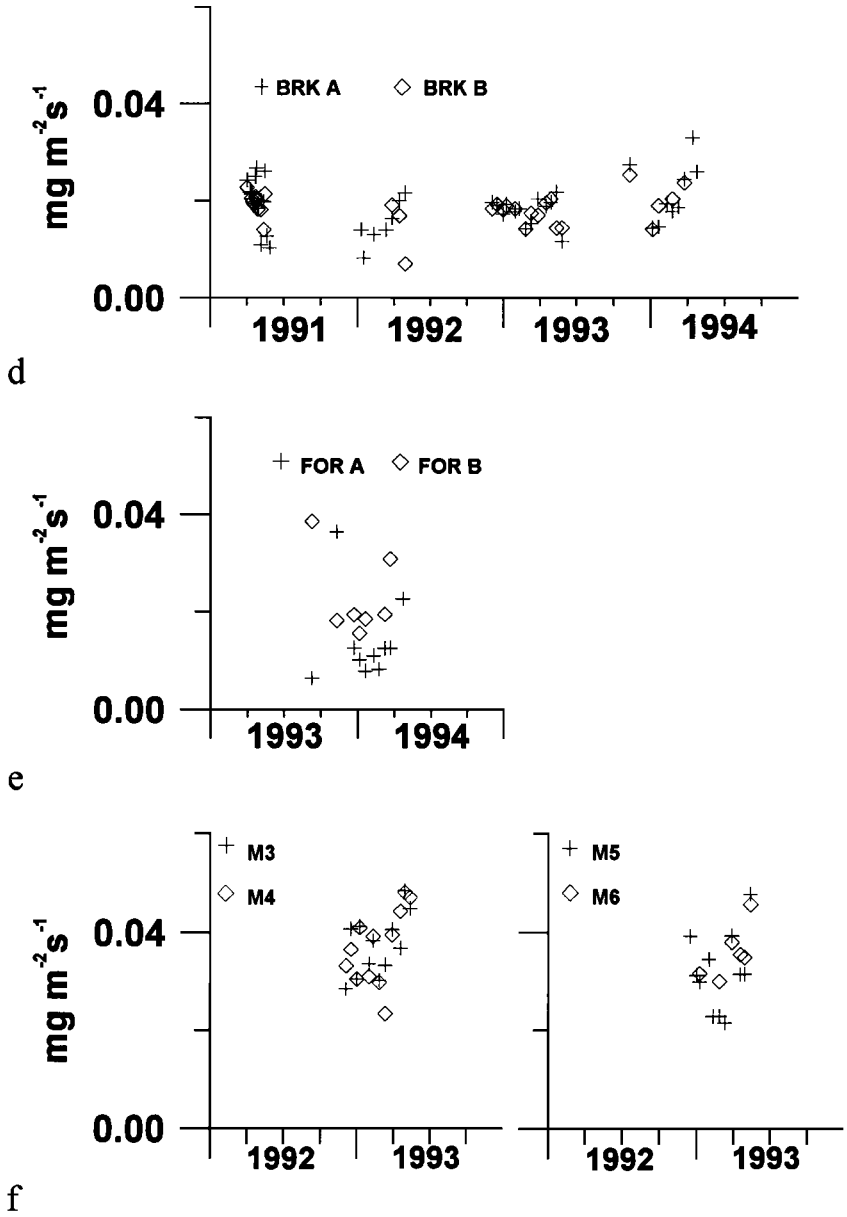

Figure 1. (continued)

M3 through M6. There is a greater temporal variation among the measurements at these four sample locations than at any but the FOR site. However, they all exhibit minima and maxima similar to those of the other sites. An average 70% rise over the minima started before the onset of melting and lasted about 6 weeks. The averages differed by almost 50% across locations probably, reflecting different soil regimes at the locations. The standard deviation of the daily differences was about 10% of the average flux, which is not significantly larger than the estimated error.

Soil concentrations. Figures 2a-2d show the temporal variation of the concentrations at the soil surface, 0.2 and 0.5 m below the soil surface. All locations at this site show a general increasing trend in concentration during each sample season. Table 3 gives the parameters of linear fits to data. For all cases the slope of the linear regression to the 0.5-m data is substantially lower than the slopes of 0.2 and 0 m. Also, R^2 for 0.5 m is lower for all these data, and the concentrations at 0.5 m are higher for most of the period. However, at the beginning of snowmelt the concentrations among the depths tend to converge. A constant concentration throughout the depth of soil, combined with the measured flux through the overlying snow, implies that there is a distributed source in the soil between 0.2 and 0.5 m.

Discussion

Temporal Variability

Longer-term temporal variability among all the locations show distinct similarities. Concentrations at the snow-soil interface increase from the start of the snow season until the

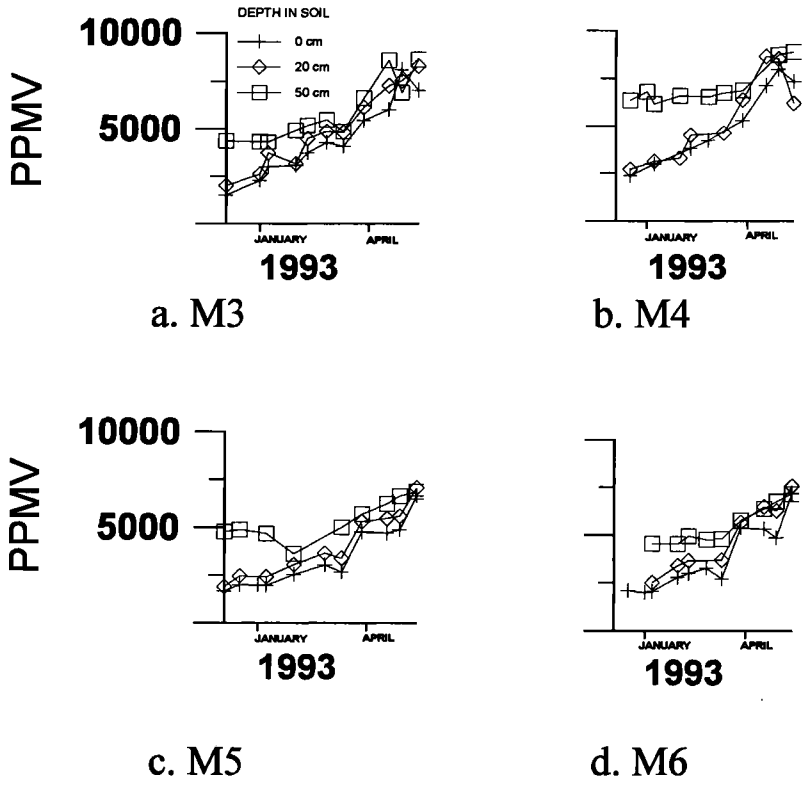

Figure 2. Temporal variation of CO_2 concentrations at the soil surface, and at depths of 0.2 and 0.5 m in the soil, at sample locations (a) M3, (b) M4, (c) M5, and (d) M6.

start of the melt season. Figure 3 shows a representative plot of concentration and snow water equivalent with the axes scaled for correspondence between the two curves. Fick's law shows that if the flux is constant, the concentration is linearly related to the snow depth and inversely related to the porosity. If the snow depth is constant, the concentration will increase with increasing snow water equivalent. Figure 3 shows that the concentration at the base of the snowpack tracks the snow water equivalent.

Table 3. Linear Temporal Trends of CO_2 Concentrations in Soil

Level, m	CO_2 Concentration, ppmv/day	R^2
	M3	
0.0	38	0.93
-0.2	38	0.95
-0.5	26	0.80
	M4	
0.0	38	0.94
-0.2	38	0.79
-0.5	16	0.70
	M5	
0.0	27	0.86
-0.2	29	0.90
-0.5	14	0.65
	M6	
0.0	31	0.83
-0.2	38	0.93
-0.5	22	0.88

Figure 2 shows that the concentration at the base of the snowpack at M3-M6 increases steadily. In contrast, the diffusional fluxes (Figure 1f) show distinct minima. The most extreme case of this behavior was at WAM A, where the concentration increased monotonically up to a maximum of 10,464 ppmv while the flux (Figure 1b) went through a distinct minimum and then a maximum. The change between the minimum and maximum was about average for this study. Thus, to a first order, control of the concentration at the snow-soil interface is the snow depth, while the flux is mainly controlled by production in the soil. In some cases, concentration increased by more than an order of magnitude from the start of snow accumulation to the time of maximum accumulation, while the flux went through a minimum and then a maximum. Second-order control of the concentration is by means of the flux from the soil. This is indicated by the fact that the concentration and snow water equivalent (SWE) plots do not track perfectly (Figure 3). If the SWE were constant, Fick's law shows that the concentration would change proportional to the flux. Data presented here show that the change could be as high as a factor of 3 over the minimum because of flux changes but that the concentration was observed to change by more than a factor of 10. It is also interesting that the very high concentration near the time of maximum flux before snowmelt at WAM A indicates that the production of CO_2 is not limited by high CO_2 concentrations up to at least 1%.

It is possible that production or consumption of CO_2 occurs in the snowpack. Such processes within the snow that affect the flux would cause flux divergence which would be evidenced by

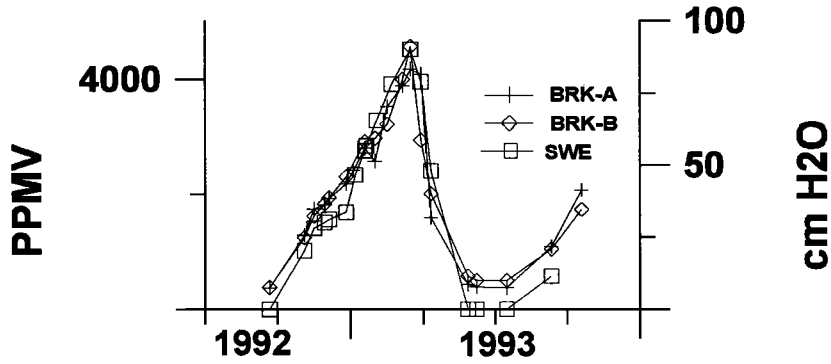

Figure 3. Concentrations of CO_2 at the snow-soil interface and the snow water equivalent at BRK, the main subalpine site.

nonlinearities in concentration profiles not related to porosity or tortuosity differences. *Sommerfeld et al.* [1993] show such evidence for the BRK (their "Subalpine") site in 1991. The production of CO_2 in the snow at that site added at most 10% to the total flux. Subsequent profiles, including profiles taken during this study, indicate that the 1991 production in the snow was an extreme event. *Mast et al.* [1994] fitted their CO_2-snow profile data with linear regressions R^2 between 0.82 and 0.99, similarly indicating little if any flux divergence in the snow.

Likewise, storage processes within the snow are not likely to be important on timescales of more than a few hours. In the dry snowpack, surface adsorption on the ice is insignificant [*Ocampo and Klinger*, 1983]. In a wet snowpack at 10% liquid water content, a cubic meter of snow with a CO_2 concentration increasing from 0 to 1000 PPMV, the storage in solution could absorb 2 to 3 hours of CO_2 at a flux rate of about 0.02 mg m^{-2} s^{-1}. Approximate calculations show that flushing of CO_2 by downward moving meltwater is about 2-orders of magnitude less than the upward fluxes we measured. *Winston et al.* [1992] measured lower fluxes from the top of the snow than from the soil. However, they hypothesized that the CO_2 was channeled along tree trunk and stem macrochannels at their site which could account for the discrepancy. This process was possible only at our FOR site, but because of drifting, the tree wells were not as well developed as those described by *Winston et al.* [1995]. These results lead to the conclusion that the main cause of temporal variability in the concentrations at the soil surface is the snow layer which forms a passive, porous cap over the sampling location but that snow processes do not affect the flux significantly on timescales greater than a few hours. In all cases the flux reaches a maximum at approximately the time the snow water equivalent reaches a maximum: opposite the behavior expected if the snowpack were controlling the flux. The diffusion model we used and the concentration profiles show that ice lenses are not a significant factor in our flux estimates.

Thus it is clear that there is a secondary cause of concentration variability which is related to temporal variability in the fluxes into the base of the snowpack. Without significant sources or sinks of CO_2 in the snow, processes in the soil control the flux. These processes were significantly different among our different sites, as would be expected. Differences between locations at each site were more variable. Sometimes they were greater than the estimated error and sometimes not.

All sites exhibit a minimum in flux early in the winter. This is in agreement with the measurements of *Winston et al.* [1995], who attributed the minimum in their measurements to low soil temperature. A flux minimum early in the winter is also apparent in the measurements of *Brooks et al.* [1995] on Niwot Ridge, Colorado. Three candidates for causing temporal variations in CO_2 fluxes from the soil are temperature changes, soil moisture changes, and population changes in the soil biota. Figure 4 shows the 5- and 20-cm soil temperatures at two sites, one near the alpine and one near the subalpine sites. After the establishment of a significant snow cover in late November, there is no significant change in the soil temperatures. These remain around -1° to 1°C, well above the approximately -6.5°C that *Coxson and Parkinson* [1987] give as a cutoff temperature for biological activity. The constant temperature lasts until the snow melts away when there is a steep rise in soil temperature. Note that the rise in CO_2 production begins before the rise in soil temperature. The temperature changes at 0.5 m, which appears to be near the source of CO_2 production, would be even smaller. Thus soil temperature changes cannot be a factor in the temporal variability of the fluxes at these sites. It is possible that air temperature changes affected root respiration at those sites where vegetation protruded above the snowpack, mainly in the subalpine. However, this could not be the case at WAM, where the snowpack was 3 m deep on January 28 and 4 m deep on February 27. The other two alpine sites were also far enough from protruding vegetation that air temperature related effects are unlikely.

No soil moisture measurements are available for these time periods. However, water vapor is transported from the soil into the snow cover during the course of the winter, driven by temperature gradients [*Smith and Boyne*, 1982]. These sites are characterized by a definite onset of melting each year, as contrasted with other climates where melting may occur several times during the winter. Moisture flows back into the soil from the snowpack when significant melting occurs. Finally, high soil moisture leads to anaerobic conditions, which limits CO_2 production, causing a decrease in flux. *Brooks et al.* [1996] observed such decreases in soil moisture at their alpine site. However, the minimum soil moisture which they observed seems too high to limit microbial activity. Furthermore, some of the rises to maxima appeared to start before there was significant melting. While the variation in CO_2 may correlate with the

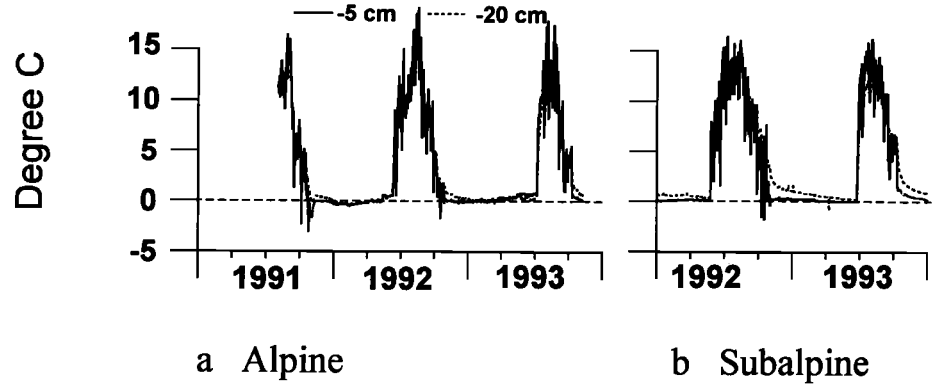

Figure 4. Temperatures at 0.05 and 0.2 m in the soil at (a) Glacier Lakes Ecosystem Experiments Site tower and (b) Brooklyn Lake Tower.

expected changes in soil moisture, this remains a speculation which should be tested.

The population dynamics of the soil biota responsible for the production of CO_2 are not known. *Brooks et al.* [1995] speculate that the variations in CO_2 flux which they observed were due to a combination of factors affecting microbial activity. We think this may be the most promising explanation.

Spatial Variability

It is apparent from Figures 1a-1f that the horizontal spatial variability on a scale of about 1 to 10 m is not very great. Table 2 lists the standard deviations of the paired differences for each sampling site for each sampling day. M3 is paired with M4, and M5 is paired with M6 for this analysis. The largest differences are for the FOR site. Here the average fluxes differ by about 50%, and the standard deviation of the differences is about 80% of the average flux for the location. This high variability may be the result of tree wells as described by *Winston et al.* [1995] or the variable snow depth observed. For the other sites the within site variations on a scale of a few meters range between 32% (HILL) and 8% (M5-M6). Thus they are of marginal significance compared to the overall accuracy of these measurements. The HILL site has a large percentage difference because its average flux is low, but the standard deviation is consistent with those at the other sites.

Zimov et al. [1993] and *Winston et al.* [1995] report much higher small-scale spatial variability. We attribute the difference in our results to the fact that our snowpacks were much deeper and of lower porosity. By impeding the vertical flux, the deeper snowpack would allow horizontal fluxes to decrease the spatial differences between the sampling locations. Our snowpacks were also flat with no macrochannels caused by tree trunks or stems, except at the FOR site. It is also possible that some of the measurements of *Zimov et al.* [1993] and *Winston et al.* [1995] were influenced by wind pumping which would have a stronger influence with thinner, more porous snow covers [*Albert and Hardy*, 1995; *Massman et al.* 1995].

Analysis of differences between sites within either the alpine or subalpine indicates that spatial variability of average flux on a scale of 10 to 100 m is within a factor of 2 (Table 2). Large-scale spatial variability over 100- to 1000-m spacing is also low, especially considering the fact that the different sites were chosen in an attempt to maximize the differences. These differ by less than a factor of 4 between the alpine and subalpine. The spatial variability between these two types of sites is complicated by the fact that they represent different ecosystems. The WGL site is, in fact, about 420 m from the HILL site, but the difference in flux is less than a factor of 2.

Errors

The measurement of gas flux across the Earth's surface has problems which have not been entirely resolved. Most studies use some type of chamber embedded in the surface. Here we have used a method whose physics is basically simple, Fick's law diffusion through a porous medium. Because this method is not directly comparable to other methods, we have given a more detailed discussion of errors than is usual. We have concluded that most of the error resides in the estimates of the snow porosity and that these errors cannot be evaluated objectively without great, and probably unwarranted, effort. Therefore we have made what we consider a fair and conservative estimate of our errors. Our error analysis indicates that estimates of CO_2 fluxes that differ by less than 15% may not be significant. However, flux differences greater than 25% are significant.

Conclusions

CO_2 flux values estimated in this study yielded equivalent annual wintertime fluxes that averaged about 95 g C m^{-2} yr^{-1} in the alpine and about 232 g C m^{-2} yr^{-1} in the subalpine sites. This compares with an annual flux range of 29 to 95 g C m^{-2} yr^{-1} for tundra and 120 to 550 g C m^{-2} yr^{-1} for boreal forest and woodland (*Raich and Schlesinger*, 1992). Since the snow-covered period can be more than 70% of the year, the winter CO_2 flux should be significant in the carbon balance in the ecosystems we studied [*Sommerfeld et al.*, 1993].

Temporal variability in CO_2 concentrations at the soil-snow interface was caused primarily by the variability in snow water equivalent of the overlying snow. Secondary variations in CO_2 concentrations were caused by variability in the flux from the soil.

Spatial variation in flux on a scale of about 1-10 m was small in this study. Average flux differences between locations at each of the sample sites were generally not significantly larger than

the estimated error. This was probably the result of the deep snowpack, which would have facilitated horizontal diffusion to decrease horizontal gradients. Differences between locations at each site were sometimes different for sampling days indicating some shorter-term flux variations. Spatial variability on a scale of 10 to 100 m was about a factor of 2. Spatial variability on the scale of 100 to 1000 m was about a factor of 4, but this seemed correlated with elevation.

Almost all of the CO_2 originates in the soil below the snow so that temporal and spatial variations in the fluxes through the snow must be caused by variations in soil production. An early winter minimum in CO_2 production was observed at all sites. The minima are similar to those observed at Niwot Ridge Colorado [*Brooks et al.*, 1996] about 150 km from the GLEES and in Manitoba [*Winston et al.*, 1995] approximately 1500 km from the GLEES. However, the cause of the early winter minimum in production is obscure. Our data did not support air or soil temperature variations as a cause. While the variation in flux probably correlates with soil moisture depletion caused by thermal gradients, the amount of depletion does not appear to be great enough to limit CO_2 production [*Brooks et al.*, 1995; *Mosier et al.*, 1993]. The role of population dynamics of the soil microbiota remains an open question.

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