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PRELIMINARY MEASUREMENTS OF CO_2 IN MELTING SNOW

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Abstract. Measurements of CO_2 near the snow-soil interface showed elevated concentrations up to 2120 ppmv. Concentrations greater than 1700 ppmv were observed 0.45 m above the snow-soil interface. The increase in CO_2 concentrations in the snow coincided with the beginning of melt. Measurements of the pH and alkalinity of the meltwater from the base of the snowpack were consistent with the measured CO_2 levels. Decreases in pH at constant alkalinity of up to 0.8 units were associated with the excess CO_2. The origin of the excess CO_2 is uncertain but may be related to litter decomposition. Elevated levels of CO_2 near the snow-soil interface at the start of melt could have important effects on meltwater chemistry, especially since streams at this time flow under a covering of snow preventing equilibration with atmospheric CO_2.

Introduction

Elevated concentrations of CO_2 have been observed in soils and snowpacks at the onset of snowmelt [Coyne and Kelley, 1974; Solomon, 1987]. Significant increases, if common, would have important effects on the chemistry of meltwater, overland flow, and soil water. Such effects would be especially significant at the time of melt initiation in the spring, because the streams flow under a blanket of snow that has accumulated for several months. Therefore, the stream water should be close to equilibrium with the interstitial air at the base of the snowpack.

We designed a gas collection system to observe the CO_2 concentrations in the soil and in the snow near the snow-soil boundary. During the 1990 melt season, we collected samples from one location at the Glacier Lakes Ecosystems Experiment Site (GLEES) at an elevation of 3280 m. The site is 55 km west of Laramie, Wyoming, in the Snowy Range. We also collected meltwater from the base of the snowpack about 200 m from the collection site using a set of long, narrow lysimeters that did not interfere with gaseous interchange with the soil [Bales et al., 1990].

Methods

The gas collectors consisted of stainless steel cylinders 100 mm in diameter and 10 mm high (Figure 1). The ends of the cylinders were covered with stainless steel mesh with openings of approximately 50 μm. One of the cylinders had one end closed with a stainless steel plate. A 1/16 NPT Swagelok fitting was inserted in the wall of each cylinder so that tubing could be attached to the collectors.

The collectors were installed in January after about 0.6 m of snow had accumulated. The soil was above freezing, with a thin (5-mm) layer of ice at the soil-snow interface. Four collectors were installed with their axes parallel to the ground. One was in the soil with its center at a depth of about 50 mm. Three were inserted into undisturbed snow from a snow pit wall; their centers were at 50 mm, 150 mm and 450 mm above the soil surface.

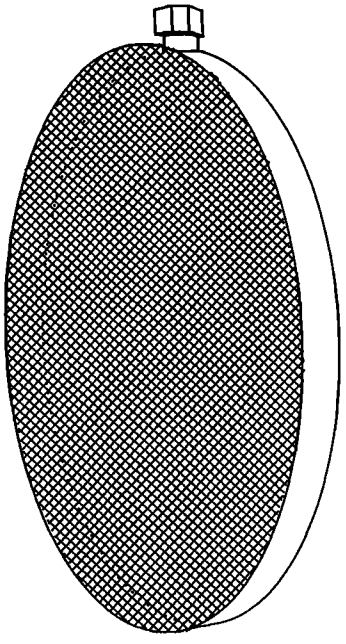

Fig. 1. Sketch of the CO_2 collector.

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A collector with one closed end was placed with its mesh end down on the soil surface in contact with a litter layer approximately 7 mm thick. A 3-m length of 1.5-mm (1/16-in.) OD teflon tubing was attached to each collector, with the other end held on a standard above the expected snow level. The snow pit was carefully backfilled with snow, and the collectors were left undisturbed for the snowpack to develop for the rest of the season.

Gas sample collection began on April 6, just prior to snowmelt when the snowpack was approximately 1.9 m thick. Snowmelt began on approximately April 10 as evidenced by melt-freeze metamorphism observed in the surface layers. Significant meltwater began to flow in snow lysimeters on April 23.

We drew samples from the gas collectors using 12-ml disposable plastic syringes fitted with plastic valves. Approximately 10 ml were drawn and discarded to completely purge the tubing, whose internal volume was approximately 1.5 ml. We obtained the first sample set using a hypodermic needle that closely fit the inside diameter of the tubing. However, because we could not be certain that the fit was airtight, when taking subsequent samples we used Swaglok attachments to insure an airtight fit. All samples were collected between 1100 and 1200 local time. In addition, we obtained samples from the air over the snow and from a tank at the site containing approximately 2000 ppmv CO_2 in dry air.

Syringes were put into Zip-Lok plastic bags for transport within 1 hr to a field laboratory at 2585 m elevation and a distance of about 12 km. At the field lab the plastic bags were filled with deionized water to preclude diffusion of any gas between the surrounding air and the syringes. A test set of samples was taken from a calibrated tank of CO_2 in air at 343 ppmv; approximately ambient concentration. Samples transported in water showed significantly less scatter than those tranported in air.

The syringes were then taken to Fort Collins, Colorado for sample analysis by gas chromatography (GC). An ultrasonic detector and Porapak Q column system were used for the GC analyses [Mosier and Mack, 1980]. The detection limit of the GC system is near 10 ppmv with a precision of 1%. Carbon dioxide concentrations are based upon calibrated gas standards from Scott Analytical.

Results

The measurements are shown in Figure 2 where measured ambient air concentrations are plotted at the height of the snow-air surface for each sample day. Each data point represents a single sample. During most of the period studied, CO_2 was elevated above atmospheric concentrations in the bottom 45 cm of the snowpack by factors of 4 to more than 6. On April 25, May 9, and May 28 the concentrations in the air above the snow were 398, 415, and 390 ppmv, respectively, indicating a possible enrichment of the atmospheric concentration from the snow.

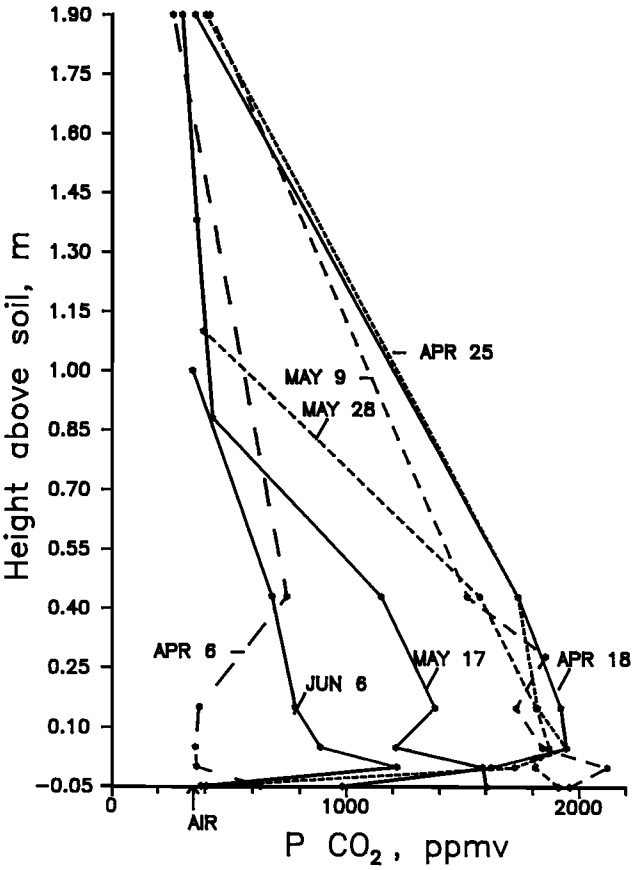

Fig. 2. CO_2 concentrations at different heights above the snow-soil interface. The concentration labeled AIR is 350 ppmv; approximately the world average. Extra points on May 17 were taken from tubing inserted into the snow.

Samples taken from the tank at the site showed that CO_2 was lost from the syringes. The tank averaged 1845 ppmv, (SD 8.6) at the Fort Collins laboratory, based on our calibration standards. Samples transported from the GLEES or from the field lab were consistently lower than this value. Tank samples taken at the GLEES and at the field lab averaged 1483 ppmv (S.D. 136) with no significant difference between the samples taken at the two locations.

On June 6 tank samples taken at the GLEES and the field lab were transported in two ways. One set of two samples was in water directly from

the deionizer; the other was in water whose CO_2 content had been increased by bubbling gas from the tank through it for 1/2 hour. The syringes in water with ambient CO_2 averaged 1377 ppmv while those in the second set averaged 1560 ppmv CO_2. This indicates that CO_2 diffused from the plastic syringes into the water, and from the water, through the Zip-Lok bags, into the atmosphere. On June 18 we collected parallel samples using the disposable plastic syringes and glass syringes with plungers sealed with mineral oil. Four samples each were collected from -50, 0, and 50 mm and the tank. The samples in the plastic syringes were about 10% lower in CO_2 than those in the glass syringes which in turn were about 10% lower than the tank which was analyzed in Fort Collins for comparison.

The points in Figure 3 are from analyses of water from snowmelt lysimeters taken during the same period as the CO_2 samples at a site approximately 200 m from the CO_2 site with approximately the same snow depth. The alkalinity was determined by means of Gran titration. The pH was generally measured within 24 hr on samples stored in sealed plastic bottles. Our laboratory and quality control proceedures are described in EPA [1987].

Discussion

The tests described above show that the relative concentrations measured on any day can be quantitatively compared but that the comparisons among different days are less reliable. For example, the -5 to 45 cm collector concentrations on May 17 and May 28 may have been essentially identical (Figure 2) although their differences represent the extreme of possible errors. The changes at .15 and .25 m from April 6 to April 18-25 and from April 18-25 to June 6 are much larger than the experimental errors. Also, the tests described above showed that the errors were systematic and proportional to the concentration with the highest collector measurements about 20% low. Thus the spread in the values was probably larger than the measurements indicate.

While the measurements are generally consistent with CO_2 generation in the litter layer, the measurements on Apr. 6, Apr. 25 and June 6 indicate that some CO_2 may have originated in the snow. Microscopic examination of a sample of snow taken near the collectors revealed the presence of significant numbers of fungi, bacteria, alga and diatoms, with filamentous predominating [R. Dufford pers. comm.]. The more specific identification of these organisms remains to be done. Generation of CO_2 in the snow would indicate active respiration by these organisms, which would in turn imply an unidentified substrate. To maintain the gradients that were measured, generation of CO_2 would have to be approximately 0.5 to 1.0 g m^{-2} CO_2 day^{-1}. This estimate is based on a simple Fick's Law calculation assuming a solid fraction of 0.5 and a diffusion coefficient for CO_2 in air of 13.9 mm^2 s^{-1}. It is consistent with the measurements presented in Soloman and Cerling [1987].

The effect of CO_2 partial pressure on meltwater pH is a function of meltwater alkalinity. The equilibrium expression of the reaction of CO_2 with water is

$$(H^+)(HCO_3^-) \; / \; P_{CO_2} = K \qquad (1)$$

where the parentheses denote activity for the ions and P_{CO_2} is the partial pressure for the gaseous CO_2. Log K is generally given as -7.81. Equation (1) combines the reaction of CO_2 with water and the dissociation of H_2CO_3 to form H^+ and HCO_3^-, so that the constant includes the Henry's law constant and the constant for dissociation of H_2CO_3. For water draining from the snowpack with very little dissolved organic carbon (average .73 ppm for 100 snow samples), alkalinity may be defined as,

$$alk = [HCO_3^-] + [CO_3^{2-}] + [OH^-] - [H^+] \qquad (2)$$

where the brackets denote concentration [Reuss and Johnson, 1985]. In these systems $[OH^-]$ and $[CO_3^{2-}]$ are insignificant and may be neglected, as may the distinction between concentration and activity (ionic strength = 10^{-4} to 10^{-5}). With these simplifications, combining (1) and (2) gives,

$$H^+)^2 + (alk)(H^+) - K\,P_{CO_2} = 0 \qquad (3)$$

Thus, for any combination of alkalinity and CO_2 partial pressure, the pH may be found from the real positive root of equation (3). as shown by the curves in Figure 3.

The estimate of 1620 ppmv CO_2 was obtained by fitting the pH-alkalinity relationship derived from Eq. (3) using a nonlinear regression procedure. The R^2 is 0.87, with most of the lack of fit attributable to the single outlier. This estimate is well within the range of the measured values, and provides an independent verification of the gas sampling measurements. The 300 and

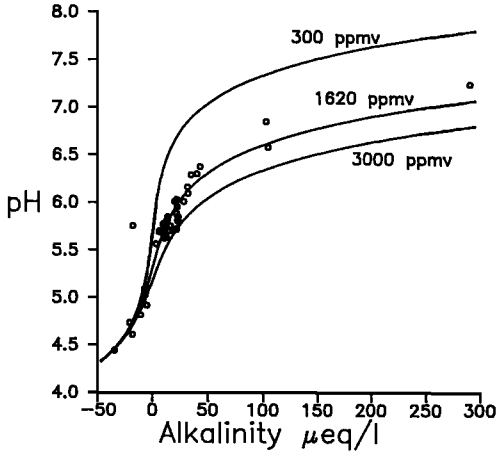

Fig. 3. pH versus Alkalinity: theoretical curves for different CO_2 concentrations (ppmv) and snow lysimeter data.

3000 ppm lines in Figure 3 are included to provide perspective on the effect of CO_2 on the relationship. A few of the alkalinity values shown in Figure 3 are in excess of 100 μeq/l, which suggests some contamination of the snowmelt by surface water [Bales et al., 1990]. However, given the nature of the relationship between pH, alkalinity, and CO_2, these points are useful in helping to establish the probable CO_2 pressure.

The presence of pH values below 5.0, coupled with negative alkalinity values, clearly shows that at some point in the melting process strong acids are being eluted from the snowpack. The percolation of waters containing elevated levels of CO_2 into and through the soil also has implications for soil solution and drainage water chemistry. The resulting H_2CO_3 is dissociated into H^+ and HCO_3^-. Much of the resulting H^+ replaces base cations on the exchange complexes. Thus, while equilibrium with elevated CO_2 decreases the pH of the soil solution, the alkalinity is actually increased. As a result of the increased alkalinity the pH of the drainage increases after equilibration with the lower CO_2 in the open atmosphere [Reuss and Johnson, 1985; Reuss and Johnson, 1986; David and Vance, 1989].

Conclusions

The results obtained and conclusion we drew from these measurements are:

Elevated concentrations of CO_2 of more than 6 times normal ambient were measured in the snow at the GLEES. The levels began to increase at the time of the onset of snowmelt.

The highest concentrations occurred at the snow-soil boundary, indicating a source in the observed litter layer. However, a source in the snow is consistent with some of the measurements.

CO_2 evolved from the snow appears to have increased the CO_2 concentration in the atmosphere over the snow, at least locally.

The snow cover at the time of initial snowmelt prevents the water from coming into equilibrium with the atmosphere, so that the meltwater is in equilibrium with the high CO_2 content and can affect the soil solution chemistry.

The pH of the snowmelt water was depressed by the elevated CO_2. However, presence of negative alkalinities and pH values below 5.0 in some samples indicates that at some times strong acid pulses are eluted from the snowpack.

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