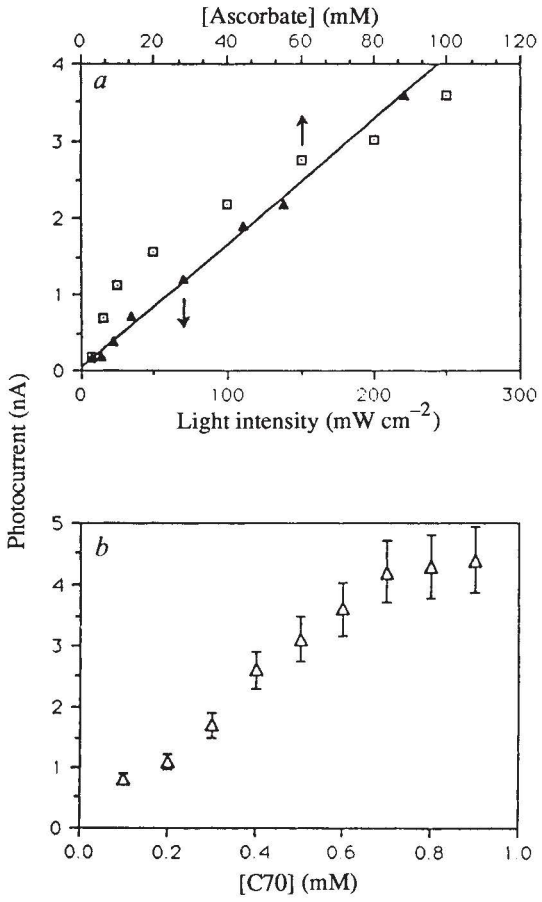

FIG. 3 *a*, Photocurrent measured as a function of ascorbate concentration (□) and incident light intensity (▲). The system consisted of [ascorbate] |0.7 mM C_{70}| 0.3 mM AQS. Either the ascorbate concentration was varied from 0 to 100 mM and the incident light intensity was constant at 220 mW cm^{-2} ($\lambda \approx 400$–600 nm), or the ascorbate concentration was constant at 100 mM and the light intensity was varied using glass filters. The photocurrent polarity and the locations of ascorbate and AQS are the same as those in Fig. 1. *b*, Photocurrent measured as a function of C_{70} concentration with 30 mM ascorbate in one aqueous compartment, 0.2 mM AQS in the other, and incident light intensity of 220 mW cm^{-2} ($\lambda \approx 400$–600 nm).

by the difficulties of transferring charge across the membrane. The use of fullerenes or of graphitic nanotubes[23], may reduce this limitation. The stability of lipid bilayers can be vastly improved through the use of microporous filters as holders[18]. The self-organizing feature of these films is a desirable characteristic for molecular electronics. □

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CO_2, CH_4 and N_2O flux through a Wyoming snowpack and implications for global budgets

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INCREASING atmospheric concentrations of the three main greenhouse gases—carbon dioxide, methane, and nitrous oxide—account for about 70% of anticipated global warming[1], but the production–consumption budgets are not balanced for any of these gases[2]. Snow can cover between 44 and 53% of the land area of the Northern Hemisphere[3] and may be several metres deep in alpine and sub-alpine regions for more than half the year. Most trace-gas budgets assume that trace-gas exchange stops when soil is snow covered or soil temperatures drop to ~0 °C (refs 4, 5). Thus alpine and sub-alpine soils are generally considered to be net sinks for atmospheric CO_2. Some reports[6,7], however, suggest that soil microorganisms beneath the snow continue to respire at temperatures close to 0 °C. Here we present evidence that the soils under alpine and sub-alpine snowpacks emit CO_2 and N_2O and take up atmospheric CH_4 throughout the snow-covered period. These fluxes represent an important part of the annual trace-gas budget for these ecosystems.

Carbon dioxide is important environmentally and biologically. It is the primary gas involved in the exchange of carbon between the atmosphere and the Earth. As a component of the atmosphere, carbon dioxide is an important greenhouse gas contributing ~45% of all greenhouse forcing[1,4]. A large amount of carbon is returned to the Earth from the atmosphere by photosynthesis and is subsequently released from biota to the atmosphere by respiration.

The contribution of CO_2 from alpine or arctic regions in winter has not been considered to be important in calculations of global carbon balances. However, high concentrations of carbon dioxide have been reported[8–10] at the base of snowpacks in arctic and temperate climates. At present, estimates of fluxes of CO_2 from natural ecosystems and from snow are incomplete, making it difficult to evaluate the controlling processes (see for example ref. 11).

Methane (CH_4) and nitrous oxide (N_2O), also important greenhouse gases, are responsible for ~20% of anticipated annual global warming[1]. Despite considerable research, large uncertainties exist in the global budget of both CH_4 and N_2O. Both gases have important soil sources, about 70% for CH_4 and 90% for N_2O (ref. 4). The observation of relatively high rates of CH_4 consumption in aerobic soils suggests an important soil sink term in the global CH_4 budget[5,12–14]. It is generally assumed that snow-covered soils do not contribute either positively or negatively to N_2O and CH_4 atmospheric budgets[4,5]. If soils below the snow remain biologically active relative to CO_2 and N_2O production and CH_4 consumption, then a portion of the annual budget of these gases may be missing in model calculations. Gas fluxes can be calculated from concentration profiles because the porosity of the snow can be estimated to within about 10% (ref. 15). Here we assume the gas flux is the result

TABLE 1 Average positive flux of gases to the atmosphere

Site	Year	CO_2 (10^{-2} mol m^{-2} day^{-1}) Flux	Range	n	N_2O (10^{-7} mol m^{-2} day^{-1}) Flux	Range	n	CH_4 (10^{-6} mol m^{-2} day^{-1}) Flux	Range	n
Sa	1991	4.6	1.8-12.4	12	8.5	2.4-23.4	8	−6.3	−16.6-−2.6	9
	1992	3.6	1.4-3.9	4	5.2	1.9-6.4	3	−2.9	−7.0-−1.5	4
Sb	1991	6.2	2.2-13.7	13	8.5	5.2-21.5	8	−15.5	−31.4-−5.8	7
	1992	4.2	3.5-5.5	4	5.9	4.4-15.7	3	−2.2	−7.4-−0.3	4
Aa	1991	1.2	1.0-3.7	10	5.0	2.8-18.8	7	−1.8	−3.4-+0.3	6
	1992	1.7	0.8-3.6	5	3.4	2.4-4.0	3	−2.2	−2.6-+0.9	6
Ab	1991	1.7	1.0-3.1	10	2.1	−0.3-5.6	7	−4.4	−9.2-+0.9	6
	1992	1.7	0.7-4.3	5	3.1	−2.3-3.8	2	−3.3	−4.8-−1.6	5

of simple, gradient-driven diffusion and a single porosity for the snow.

The sampling locations for this study were in the Glacier Lakes Ecosystem Experiments site (GLEES) in the Snowy Range of southeastern Wyoming, west of Laramie at about 41° 20′ N, 106° 20′ W. Samples were taken from two alpline sites (Aa, Ab) and two sub-alpine sites (Sa, Sb). The alpine sites, separated by about 10 m, are at the ecotone between alpine and sub-alpine, at an elevation of 3,286 m. The location is on an exposed, rocky ridgetop with little soil development, and has sparse alpine vegetation with small, widely scattered trees. The sub-alpine sampling sites, separated by about 3 m, are in a small opening in a sub-alpine spruce-fir forest at an elevation of 3,182 m. This location is a typical sub-alpine meadow. Geology, soils, vegetation and topography details of GLEES are given in ref. 16.

Gas collectors[7] were installed in the ground at 15 cm below the surface, at the surface, and in the snowpack at 5, 20, 50 and 100 cm above the ground at each site. Samples were drawn using 20-ml nylon syringes fitted with two-way nylon stopcocks. Serum bottles (20 ml), capped with butyl rubber stoppers, were evacuated and filled for transport to the Fort Collins Agricultural Research Service laboratory for N_2O analyses and for CH_4 analyses in 1991. Another 20 ml were drawn and the syringes brought to a field laboratory ~10 km from the sample locations, for analysis of CO_2 and CH_4 (1992) by gas chromotography within five hours of sample collection. The 1991 N_2O and CH_4 samples were stored for periods up to 3 months before analysis by gas chromatagraphy[17,18].

Up to seven depths were sampled for each of the four sites between 2 April and 28 May 1991 and between 12 March and 14 May 1992. The sampling intervals were between 1 and 7 days in 1991 and roughly every 14 days in 1992. Figure 1 shows the average concentrations of CO_2, N_2O and CH_4 in the snow and ground during the sample periods, at the four sites.

The average CO_2 profiles are in good agreement with the preliminary results of ref. 7. In contrast to those measurements, the initial samples showed high CO_2 concentrations at all levels indicating that respiration was occurring before appreciable melt water flowed from the snow. We attribute the difference to poor sampling technique in the initial samples used in ref. 7. The CH_4 concentrations for 1991 are less accurate than the 1992 data because of storage problems.

On 7 May 1991, a snow pit was dug near the sub-alpine location to obtain an estimate of the snow porosity. The snow depth at the pit was 205 cm, about 50 cm deeper than at the two sub-alpine sample sites. However, the stratigraphy did not show any large changes in porosity. Discontinuous ice lenses were located at 143, 158 and 184 cm. The thickness-weighted average porosity of the upper 100 cm of snow was ~0.58. For most of the profiles, gradients in the layer above 100 cm are similar to or smaller than those from 50 to 100 cm (Fig. 1). This indicates that the ice lenses did not have a significant effect on the flux. Furthermore, it is our experience that ice lenses disappear early in the melt process after the snow contains a significant amount of liquid water. Snow pits in 1992 indicated that the upper snow layers had similar porosities.

Because biological activity was suspected in the snow, the pit dug on 7 May 1991 was sampled for biological material. The profile of the combined counts of fungus, algae and bacteria showed a strong peak at 50 cm, corresponding to the inflection point in the CO_2 and N_2O profiles. Fungus filaments and spores formed the main fraction of the biota sampled.

Table 1 gives calculated fluxes of the gases at each site. They were calculated assuming simple diffusion, average gradients from 100 cm to the surface, average snow depths estimated from limited measurements and an average porosity in the top layer from the snow pit. Because the snow pit was dug later in the season after the snow had compacted, the calculated fluxes are probably conservative.

$$J_g = D_g(\mathrm{d}[g]/\mathrm{d}z)f$$

where J_g is the gas flux, $\mathrm{d}[g]/\mathrm{d}z$ is the vertical concentration gradient and f is the porosity. The diffusion coefficient D_g was 0.139 cm^2 s^{-1} for CO_2 and N_2O and 0.22 for CH_4, an experimental value for CO_2 and estimated values for the other gases[19]. Molar volumes of the gases were corrected for temperature and pressure. Replications and calibrations indicate that the concentration data are accurate to ±3% for CO_2 and for CH_4 in 1992. This is the precision of the measurements of N_2O and of CH_4 in 1991 which, because of longer storage, are thought to have an accuracy of about ±10%. The ranges of the data and the numbers of samples are also shown in Table 1.

The soil temperatures at 20 cm below the soil surface in a forest clearing about 0.5 km from the alpine location dropped below 0 °C in mid-November and slowly decreased to −0.2 °C. At the sub-alpine location, soil temperatures at 20 cm dropped to 1.5 °C in mid-November and decreased to 0.5 °C before the mid-June snowmelt when the soil temperature increased rapidly at both sites. Although soil temperature remained within ~1 °C of freezing during the sampling period, soil microbial activity did not cease. The soil continuously served both as a source of CO_2 and N_2O, which evolved to the atmosphere through the snow, and as a sink for atmospheric CH_4. As the main biological activity was in the soil and the soil temperature did not change much during the entire winter, we believe the results from the sampling periods are representative of the entire winter.

The amount of carbon mobilized as CO_2 at the sub-alpine sites ranges from 2.9 to 14.5 mol m^{-2} for a snow-covered period of 235 days. Litter fall in a lodgepole pine forest near our sites was estimated to contribute between 4.45 and 7.43 mol m^{-2} yr^{-1} (ref. 20). Litter fall should be considerably lower in our non-forested sites. The total amount of carbon fixed in temperate forests in the United States is estimated to be 13.3 mol m^{-2} yr^{-1} (ref. 21, 22). Less carbon would be fixed at high elevation locations such as those we sampled, as low temperature, short growing season and low light levels under the snow cover limit production. Although these comparisons are approximate, they show that the amount of carbon respired in the winter in snow-covered environments can be an important fraction of the total carbon budget.

The profiles also indicate that respiration occurred in the snow at about the 50-cm level in 1991. Respiration in the snow may be related to the high fungus and bacterial counts at this

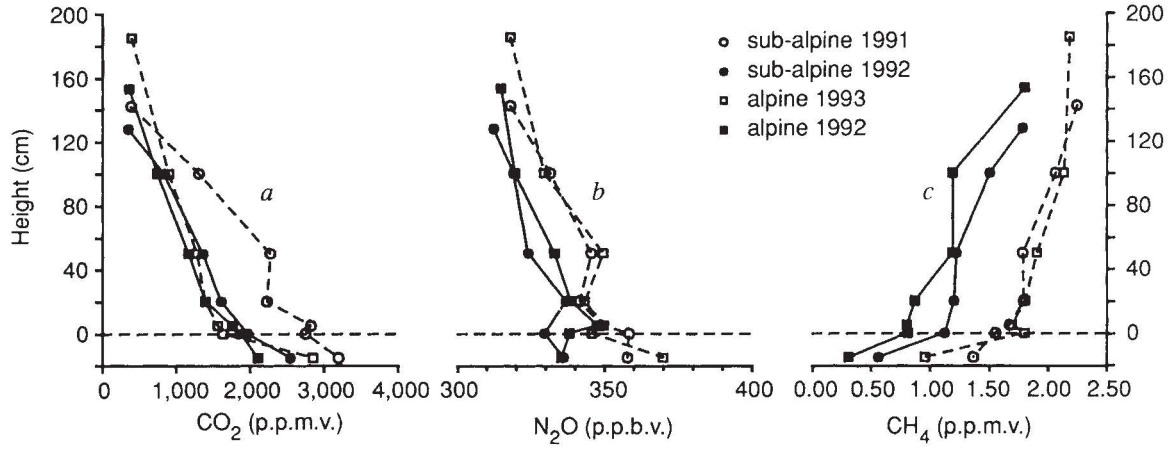

FIG. 1 Average concentrations of CO_2 (*a*), N_2O (*b*) and CH_4 (*c*) in the snow at four sites for the periods sampled in 1991 and 1992.

level. CO_2 production in the snow significantly increased the flux at sub-alpine sites in 1991 but not in 1992 or at the alpine sites.

During the summer of 1991, between mid-June (when the snow cover melted) and mid-October (when the snow cover returned), N_2O and CH_4 gas fluxes were sampled over a meadow located ~50 m from the sub-alpine location. N_2O emissions, measured at 1- to 7-day intervals, averaged 1.34×10^{-7} mol m^{-2} d^{-1} during the 130-day collection period (A.R.M., L. K. Klemedtion, R.C.M. and R.A.S., unpublished data). The N_2O emissions through the snow averaged 7.0×10^{-7} mol m^{-2} d^{-1} at the sub-alpine location and 3.4×10^{-7} mol m^{-2} d^{-1} at the alpine location over a 235-day period.

We estimate CH_4 flux from the atmosphere to the soil under the snow to be 6.7×10^{-6} and 2.9×10^{-6} mol m^{-2} d^{-1} at the sub-alpine and alpine locations respectively. In the adjacent meadow, CH_4 flux into the soil averaged 7.4×10^{-6} mol m^{-2} d^{-1} throughout the snow-free period (A.R.M., L. K. Klemedtion, R.C.M. and R.A.S., unpublished data). These data suggest that the soil serves as a larger CH_4 sink while under the snowpack (235 days) than during the snow-free time (130 days). In the Colorado short grass steppe during the winter, when no snow cover existed and soil temperature was <-2 °C, the soils continued to take up CH_4 from the atmosphere at the rate of $6.8\text{–}13.6 \times 10^{-5}$ mol m^{-2} d^{-1} (ref. 13).

Our data show that the soil microflora are active even when they are snow-covered and near 0 °C. N_2O is produced as a result of nitrification and denitrification in soil processes that proceed at higher rates at higher temperature, but have been observed at −2 °C in supercooled soil[23]. Emissions from the soil through snow continued throughout the period of snow cover. Methane uptake under the snow seems to represent a considerable portion of the CH_4 flux during the year. Soil respiration under the snow continued through the sampling period and represents oxidation of more than 25% of the estimated carbon fixed in the ecosystem during the growing season. Soils having surface horizon temperatures near the freezing point represent a considerable fraction of the land surface in the Northern Hemisphere during the winter[3]. The fact that similar concentrations of CO_2 have been measured at the bases of snowpacks in Utah[10] and Fairbanks and Barrow, Alaska[8,9], indicates that similar fluxes occur in these widely spaced, dissimilar regions. Observations[6,8–11,14] indicate that the data presented here are representative of such systems and that the winter fluxes of CO_2, N_2O, and CH_4 are important in the global budgets of these gases. □

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Numerical simulation of self-organized stone stripes

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GEOMETRICALLY regular stripes of stones are found on many unvegetated alpine and polar hillslopes; known as 'sorted stripes' because of the characteristic textural sorting between surface stones and fine-grained soil, they contrast markedly with the lack of order typical of natural landscapes. The spacing of the stripes can range from centimetres to metres (about 10–20 times the average stone diameter[1,2]), with individual stripes extending downslope for many tens of metres (Fig. 1). A variety of formative mechanisms have been proposed[3], but it is still unclear how such orderly stripes can arise spontaneously, and what dictates the spacing. Here we present two-dimensional computer simulations in which the displacement of surface stones is governed by the preferential growth of needle-ice in stone-free regions of soil during each freezing cycle. Regular patterns of stones and soil that closely resemble natural stripes are found to emerge spontaneously from the model as a result of identifiable feedbacks between soil texture, ice growth and local slope.

The recurrent frost-induced displacement of surface stones is a primary characteristic of hillslopes mantled by sorted stripes.