

Carbon monoxide as a tracer of gas transport in snow and other natural porous media

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[1] The movement of air in natural porous media is complex and challenging to measure. Yet gas transport has important implications, for instance, for the evolution of the seasonal snow cover and for water vapor transport in soil. A novel *in situ* multi-sensor measurement system providing high-resolution observation of gas transport in snow is demonstrated. Carbon monoxide was selected as the tracer gas for having essentially the same density as air, low background concentration, low water solubility, and for being detectable to ≤ 1 ppmv with small, low-cost, low-power sensors. The plume of 1% CO injections 30 cm below the snow surface was monitored using 28 sensors (4 locations, 7 depths). The CO breakthrough curves obtained at distances of 0.5–1 m were in good agreement with a simple analytical advection-diffusion model. The tracer system appears suitable for a wide range of applications in experimental soil science and hydrology addressing moisture transport and evapotranspiration processes. **Citation:** Huwald, H., J. S. Selker, S. W. Tyler, M. Calaf, N. C. van de Giesen, and M. B. Parlange (2012), Carbon monoxide as a tracer of gas transport in snow and other natural porous media, *Geophys. Res. Lett.*, 39, L02504, doi:10.1029/2011GL050247.

1. Introduction

[2] Transport of gas in natural porous media is complex and has important implications for the evolution of snow cover via sublimation and condensation [e.g., Parker and Thorpe, 1995; Hood et al., 1999; Box and Steffen, 2001; Albert, 2002; MacDonald et al., 2010], the rates of microbial processes, soil-atmosphere gas exchange, and evaporation from soils [e.g., Parlange and Katul, 1992; Parlange et al., 1998; Heitman et al., 2008; Williams et al., 2009; Heitman et al., 2010]. Some methods to measure gas diffusivity in soil have been developed and applied in soil science. Laboratory methods typically use diffusion chambers [Glauz and Rolston, 1989; Rolston and Moldrup, 2002; Allaire et al., 2008; Hamamoto et al., 2009; Lange et al., 2009], while field methods aim at *in situ* measurements without disturbance of the soil structure [McIntyre and Philip, 1964;

Lai et al., 1976; Rolston et al., 1991; Werner et al., 2004; Schwen et al., 2011].

[3] There are two principal mechanisms causing gas advection in porous media (e.g., snow): quasi-static pressure gradients across surface roughness elements in the presence of a mean wind, and fast pressure fluctuations as a result of atmospheric turbulence. Earlier theoretical, model, and experimental studies identified atmospheric pressure fluctuations as a forcing mechanism for advective flow in porous media such as snow [e.g., Colbeck, 1989; Clarke and Waddington, 1991; Albert and McGilvary, 1992; Cunningham and Waddington, 1993]. More recent work confirmed the direct relation between rapid atmospheric pressure fluctuations and gas exchange rates with the underlying porous media [e.g., Massman et al., 1997; Albert and Hawley, 2002; Neumann and Waddington, 2004; Takle et al., 2004; Severinghaus et al., 2010]. Other studies deal with the advective transport of natural CO₂ in porous media [e.g., Massman, 2006; Massman and Frank, 2006] and relate air movement in snow to fluctuations of atmospheric pressure. However, both static pressure differences as well as pressure fluctuations in time, for instance due to high-frequency atmospheric turbulence, act as a driving force for air movement in snow [Massman et al., 1997; Bartlett and Lehning, 2011]. The objective of this paper is to introduce a novel, *in situ* method for tracing gas movement through natural porous media suitable for numerous applications in soil science and hydrology.

[4] To date, the primary experimental method to assess *in situ* gas transport within natural porous media has been the injection of a tracer gas, followed by periodic sample extraction, with off-line analysis in a laboratory setting [e.g., Albert et al., 2002]. This has limited the temporal and spatial resolution due to the mechanical limitations of withdrawal and storage of samples, which may also influence the movement of the resident gas. Sampling ‘blindly’ with respect to the tracer movement, i.e. concentrations are not known in real time, can also lead to non-optimal sampling frequency and distribution. Thus, for high-resolution *in situ* studies of gas transport it is advantageous to install measurement devices in the field and monitor the transport without gas extraction.

[5] In the selection of a tracer gas, the following requirements are critical: neutral buoyancy (achieved either by using extremely low concentrations (e.g., SF₆ [Albert and Shultz, 2002]), or by choosing a blend of gases with density equal to the resident gas); conservative (minimal partitioning to the solid or liquid phase or degradation in the time frame of the study), easily detectable without affecting the processes under study, and with low atmospheric background concentration and few cross-interferences to allow

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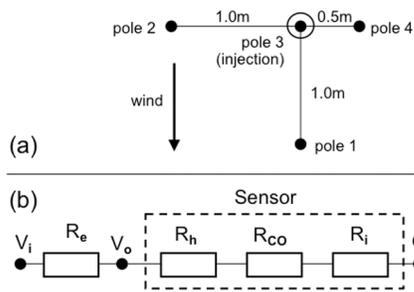


Figure 1. (a) Configuration of sensor poles in the field (top view) and (b) the equivalent circuit series resistance model for CO sensors. R_e and R_i denote external and internal resistors, R_h and R_{CO} denote variable internal resistances varying with humidity and CO concentration, respectively. V_i and V_o are the supply and output voltages, and G denotes ground.

reliable detection of tails of breakthrough. The sensors required should be small to minimally disturb native air movement, fast response, consume minimal power so as not to alter the thermal regime (also useful for locations where power is limited), easily detect gas at very low concentrations so that the lowest volume of tracer gas needs to be injected, and easy to install to allow for multiple points of observation. Carbon monoxide was selected as a gas tracer for application to the study of gas movement in snow and other natural porous media for these reasons, specifically having the following traits:

1. CO is neutral buoyant. At 0°C , 1 atm, the density of pure CO is 1.25 kg/m^3 (versus dry air at 1.29 kg/m^3). A 1% CO/air mixture has a density within 0.04% of that of air.
2. CO has low atmospheric background concentrations (typically 0.05–0.20 ppmv).
3. CO has low water solubility. At standard conditions of temperature and pressure, the solubility in water is 0.026 g/l, similar to that of helium (0.015 g/l). An upper bound on the aqueous dissolved fraction of the tracer is $<0.1\%$ based on the Henrys law coefficient ($9.5 \times 10^{-4} \text{ mol/l/atm}$, and a water content of $0.1 \text{ m}^3/\text{m}^3$, typical of soil water content (much lower for snow)).
4. CO is not rapidly consumed by most sub-surface microbial communities [e.g., Conrad et al., 1981].
5. CO is readily available and affordable.
6. CO, at tracer concentrations used in this study, is readily safely handled outdoors.
7. Highly sensitive (0.5–10,000 ppmv), compact (8 mm), low power ($<35 \text{ mW}$), inexpensive ($<\text{USD } 20$) CO sensors have recently become widely available.

[6] The objective of this study was to demonstrate the feasibility of carbon monoxide (CO) as a tracer of gas transport in porous media. This was achieved through a field trial of a suite of *in situ* CO sensors in an alpine snow pack.

2. Methods

2.1. Experimental Setup and Sensor Calibration

[7] Measurements were taken in a seasonal alpine snow pack at the Plaine Morte glacier near Crans-Montana, Switzerland, at 2775 m altitude during the winter of 2007. During the experiments the mean wind speed was generally low ($<3 \text{ m/s}$) and the snow pack relatively dense ($\approx 360 \text{ kg/m}^3$). Four 1m-long tapered sensor poles were

installed, each equipped with seven carbon monoxide sensors spaced at 15 cm with the uppermost sensor just above the snow surface. The goal was to have a central injection and sampling pole surrounded by three other sampling poles (Figure 1a) although several other meaningful configurations were possible. Here we employed AppliedSensor MLC devices, rated for a concentration range of 0.5 to 10,000 ppmv CO in air, though many other brands of devices have similar specifications, and may have superior characteristics in other respects (e.g., cross-sensitivity to humidity). A volume of 500 ml of gas was injected and the CO sensors were sampled at 10 Hz, recording one-minute averages of the 600 values. Details on the sensor pole design and injection procedure are provided in the auxiliary material Figure S1.¹ To represent ambient conditions, an *in situ* calibration of the sensors (required to translate the sensor output voltage to a corresponding trace gas concentration) was performed at CO concentrations of 5, 500, and 10,000 ppmv (see auxiliary material Text S1 for details).

2.2. Analytical Modeling

[8] To confirm the validity of the sensor output, and to interpret the data, a mass-conserving three-dimensional Gaussian solution of the advection-dispersion equation for an instantaneous point injection in a homogeneous media (largely true for this mid-winter snow-pack) was employed [e.g., Simunek et al., 1999]. The governing advective-dispersive equation for CO concentration is

$$\theta \frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{u}C) - \nabla \cdot (\mathbf{D} \cdot \nabla C) = 0 \quad (1)$$

where θ [–] is the air-filled snow porosity, C [kg m^{-3}] is the concentration of CO, \mathbf{u} [ms^{-1}] is the velocity of air in the snow (with component speeds of u , v , w in the x , y , and z directions), and \mathbf{D} [m^2s^{-1}] is the dispersion tensor. The injection is modeled to have taken place at a distance d above the impermeable ice surface in a snow pack of depth h . The concentration at the snow/atmosphere boundary was taken to be zero, while the ice glacier surface was taken to be a no-flux boundary. Since the governing equation is linear, superposition of solutions was used to satisfy no-flux and zero concentration boundaries, which requires the addition of virtual plumes of specific characteristics with the analytical solution:

$$C(x, y, z, t) = \frac{M}{\theta(4\pi t)^{3/2}(D_x D_y D_z)^{1/2}} * \left[\exp\left(-\frac{(x-ut)^2}{4D_x t} - \frac{(y-vt)^2}{4D_y t} - \frac{(z-d-wt)^2}{4D_z t}\right) + \exp\left(-\frac{(x-ut)^2}{4D_x t} - \frac{(y-vt)^2}{4D_y t} - \frac{(z+d-wt)^2}{4D_z t}\right) - \exp\left(-\frac{(x-ut)^2}{4D_x t} - \frac{(y-vt)^2}{4D_y t} - \frac{(z-(h+d)-wt)^2}{4D_z t}\right) \right], \quad (2)$$

where M [kg] is the mass of CO injected at depth d . The x -axis is positive downwind (i.e., $v = w = 0$), thus the off-

¹Auxiliary materials are available in the HTML. doi: 10.1029/2011GI050247.

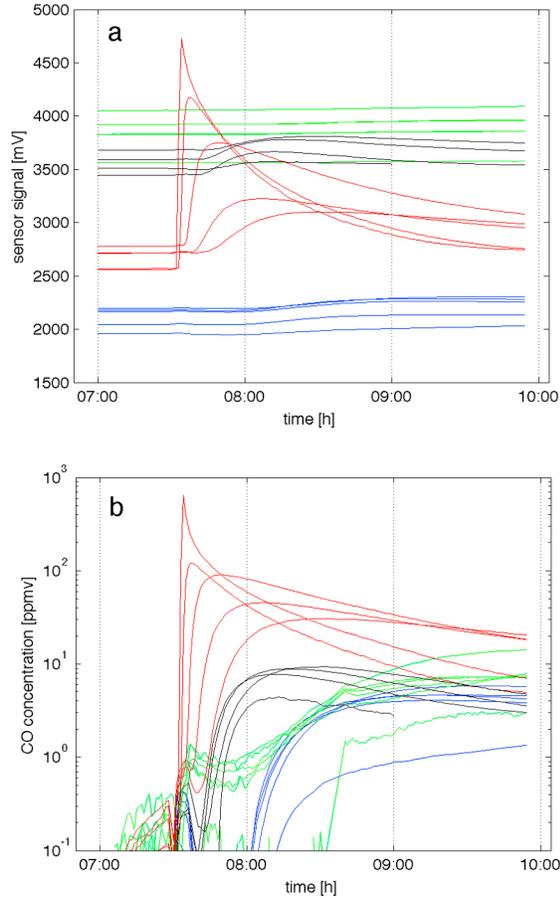


Figure 2. Breakthrough curves at each sensor location: (a) raw data and (b) calibrated CO concentration (semi-log scale). Colors denote sensor poles as follows: blue: P1, 1 m downwind, green: P2, 1 m lateral, red: P3, injection, black: P4, 0.5 m lateral (cf. Figure 1). Curves are shown for the 15, 30, 45, 60, 75, and 90 cm levels; surface level and malfunctioning sensor data have been removed. The 0.1 ppmv cut-off in Figure 2b is the expected atmospheric background concentration.

diagonal terms of the dispersion tensor are zero. For the purpose of this paper we will approximate the solution to explicitly describe only diffusion. This may somewhat under-estimate the spreading in the direction of advection, but will not change the estimated advection velocities based on center-of-mass. A Péclet number $Pe \approx 5$ (see section 3.2.) indicates that also advection contributes to the lateral transport. In this simplified framework, all points on an x-y-plane with the same radial distance from the center of mass of the plume are modeled to have equal tracer concentrations.

[9] The free air diffusion coefficient for CO was calculated following the kinetic theory of gases accounting for the ambient pressure and temperature at the field site as $D_{CO} = 2.56 \times 10^{-5} \text{ m}^2/\text{s} \pm 1\%$. The tortuosity ψ was set equal to 0.66, which is in the range of common values reported for snow [e.g., *Massman et al.*, 1997; *Albert and Shultz*, 2002], and a porosity θ of 0.61 results from the mean density of the top 1 m of the snow pack being $360 \text{ kg}/\text{m}^3$. Consequently,

the effective diffusion coefficient ($\psi \theta D_{CO}$) is estimated to be $1.03 \times 10^{-5} \text{ m}^2/\text{s}$, which is about two times the effective diffusion coefficient of SF_6 through similarly compacted snow [*Albert and Shultz*, 2002].

3. Results and Discussion

3.1. Sensor Calibration

[10] Both absolute humidity and CO concentration influence the electrical resistance of the sensor: The devices present a series electrical resistance that increases linearly with increasing concentration of either constituent (humidity, R_h , and CO, R_{CO}), as well as a fixed internal resistance, R_i . If the system is energized with a voltage V_i , and an output (V_o) of the device is measured at the junction with the external resistor (R_e) (Figure 1b), from Ohm's law one can compute

$$R_{CO} = \frac{R_e}{1 - (V_o/V_i)} - R_e - R_h - R_i. \quad (3)$$

The manufacturer reports that the sensor acts as a series system, with the resistance due to changes in CO concentration being linear with concentration and independent of changes in resistance due to temperature or humidity. Thus, we take the CO and humidity effects on resistance to be linear,

$$\begin{aligned} R_{CO} &= aCO \\ R_h &= bH \end{aligned} \quad (4)$$

where CO and H are the concentrations of carbon monoxide and of water vapor (absolute humidity), respectively. After substitution and solving for CO we find

$$CO = \frac{1}{a} \left(\frac{R_e}{1 - (V_o/V_i)} - R_e - bH - R_i \right), \quad (5)$$

which, collecting constants and coefficients, may be written as

$$CO = \frac{d}{1 - (V_o/V_i)} - e, \quad (6)$$

where the calibration parameter $d = R_e/a$ is a system constant and $e = -(R_e + bH + R_i)/a$ is a humidity dependent quantity. To calibrate for d and e requires the system to be run at the particular humidity expected for the experiment under at least two CO concentrations, one of which could be zero. In our experiments the value of d was determined from the slope of the 5 and 500 ppmv *in situ* calibration data while the value of e was determined by the sensor value immediately prior to injection, when $CO = 0$ ppmv.

3.2. Point Injections

[11] Carbon monoxide was injected 30 cm below the snow surface and its concentration in space and time was monitored. The built-up pressure due to the injection propagates with the speed of sound over distances of <1 m. The injection fills initially a sphere with a radius <6 cm and quickly displaces the resident air into an area beyond this volume and will not contribute to CO dispersion on the time scale of minutes. Breakthrough curves showing raw sensor output

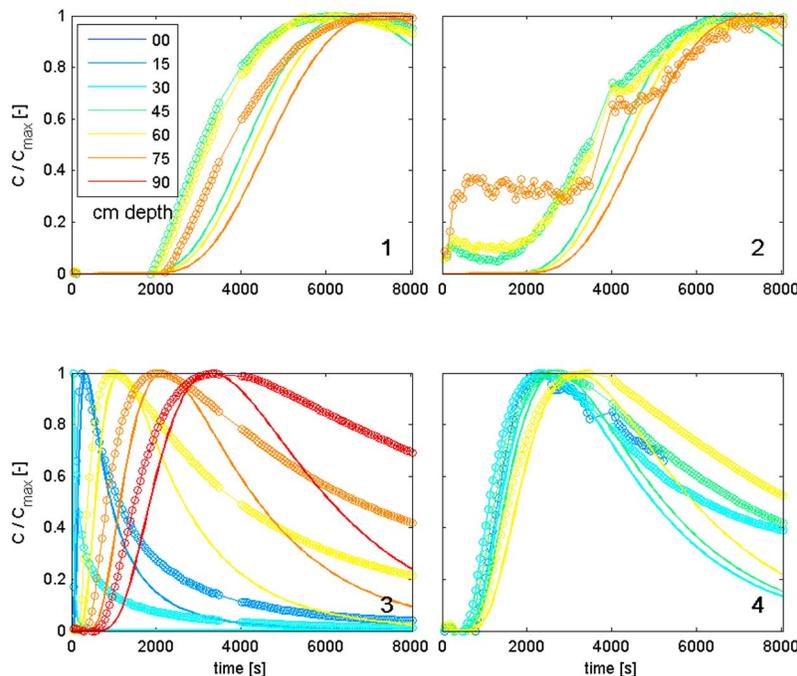


Figure 3. Breakthrough curves of scaled CO concentrations from sensors (circles) and from model data. Sensor depth is measured in centimeters from the surface; observational data are shown with circles, fitted solutions as solid lines. The following sensors have been removed: four observational surface levels, several malfunctioning sensors, and sensors where the peak concentration arrived later than the end of measurements (8000s after injection). Numbers in the bottom right corners correspond to pole numbers (cf. Figure 1a): 1 m downwind (1), 1 m lateral (2), injection (3), 0.5 m lateral (4). The best-fit effective diffusion coefficient for the simulations was $1.03 \times 10^{-5} \text{ m}^2/\text{s}$, and the advective velocity in the downwind direction was $1.2 \times 10^{-4} \text{ m/s}$.

and calibrated CO concentrations for each sensor illustrate the typical shape of an evolving Gaussian seen from a fix point, with measured concentrations spanning over 4 orders of magnitude (Figure 2). Since the range of meteorological and snow conditions during the period of experiments was narrow only one exemplary case is shown. Also, some experiments appeared unfavorable for analysis due to strong variations in the mean wind speed or major changes in wind direction (advecting the plume away from some sensor poles). To better understand the behavior and significance of forced advection in snow (or soil/sand), measurements at a wider range of meteorological and snow conditions would be desirable.

[12] The calibration curve for each sensor might be expected to become non-linear at very high concentrations where the CO sensors might saturate. This was tested by computing the value of the d -parameter (cf. equation (6)) independently for pairs of 0, 5, 500, and 10,000 ppmv. Averaging across all sensors, the d -values for our system were 47.3 ($\sigma = 28$), 55.3 ($\sigma = 28$), and 366.7 ($\sigma = 245$), respectively. The observed spread is expected since factory calibrated sensors also show large differences in signal level for a given CO concentration. The sensors appear to be close to linear over the 5–500 ppmv range (equal to specified sensor sensitivity range), becoming less responsive at the higher concentrations, as would be expected. If very high concentrations are expected, a curvilinear calibration could be employed to retain accuracy over the extended range. In our study, only one point exceeded 500 ppmv, and then by

just 20%, so the linear model is sufficient for the purpose of proof-of-concept.

[13] Since the maximum concentration at the injection point and other locations close to it is generally several orders of magnitude larger than the maximum concentration of the dispersed plume at points more distant from the injection point, sensor signals have been scaled to a unit interval for ease of graphical comparison,

$$\tilde{C} = C/C_{\max}, \quad (7)$$

where C is the calibrated CO concentration at a given time, and C_{\max} is the peak concentration seen at that sensor.

[14] Breakthrough curves for each sensor pole location using the best match of advection velocity of $1.2 \times 10^{-4} \text{ m/s}$ in the simulation are shown in Figure 3. In general, we find a good agreement between the measured and simulated breakthrough curves. Differences are seen at the tails of the breakthrough curves with the measured concentrations always higher than the simulated curves, suggesting that the actual spreading exceeded that expected by diffusion. This consistent pattern indicates the presence of some mechanical dispersion, as would be expected of a wind-driven gas movement through snow, and inclusion of mechanical dispersion would be needed to better fit the data, as found by *Seok et al.* [2009]. Taking a characteristic length of 1m (about the distance over which we measure), the diffusivity of CO in air at local ambient conditions ($2.56 \times 10^{-5} \text{ m}^2/\text{s}$), and the observed advection velocity ($1.2 \times 10^{-4} \text{ m/s}$), a

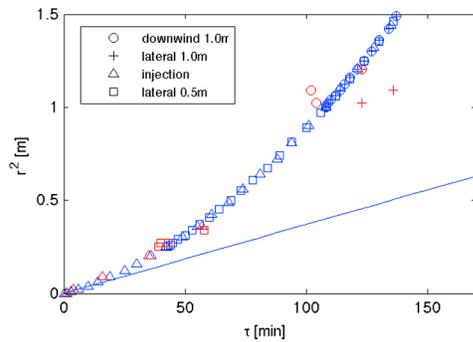


Figure 4. Relation of the squared radial distance of a sensor from the injection point to the breakthrough time of the concentration peak (blue: model, red: measurements). Only sensors with a well behaved breakthrough curve (cf. Figure 3) are shown. The straight line represents the analytical solution for an advection velocity equal to zero. The slope of this line is equal to the proportionality factor, $6D$, for the $\tau-r^2$ relation, cf. equation (6).

Peclet number $Pe < 5$ results, indicating that advection is contributing to the longitudinal spreading of the trace gas, with diffusion and advection rates of the same order of magnitude. However, when estimating mechanical dispersion as the product of the pore velocity and the mean pore size [Liao and Tan, 2008] with ~ 1 mm for snow, the resulting dispersion of $\sim 10^{-7}$ m²/s remains ~ 2 orders smaller compared to the molecular diffusion coefficient D_{CO} even when reduced by the tortuosity. The advection velocity in the snow is expected to be a function of the mean wind speed and the near-surface turbulence characteristics and will certainly depend on snow properties such as density and matrix geometry. The advection velocity of 1.2×10^{-4} m/s determined in our example experiment, is very small as a result of the ambient atmospheric and snow conditions at that time. At higher wind speed, turbulence intensity, and for fresh, low-density snow, the advective component and mechanical dispersion are expected to be more important representing a significant flux term which would suggest precise plume modeling should include hydrodynamic dispersion. The complex interplay of parameters and processes points out the value of high spatial and temporal resolution in-situ sensing in the study of gas transport processes.

[15] In a 3-D isotropic and unbounded case, and in absence of advection, the breakthrough time, τ , i.e. the time since injection when the maximum concentration is measured at a given point, is proportional to the square of the radial distance, r , from the injection point,

$$\tau = r^2/6D, \quad (8)$$

with D being the diffusion coefficient, which provides a scaling factor for each of the points of observation to allow plotting on a common axis. While useful for the geometry of the field experiment here, equation (8) is not strictly appropriate over travel distances greatly in excess of the depth of the snowpack (since the problem then becomes asymptotically two-dimensional).

[16] The relation of calculated breakthrough times at all sensor locations to the corresponding squared radial

distances is shown in Figure 4, both for the experimental and model data. Model data computed considering an air advection velocity in the snow of 1.2×10^{-4} m/s are in good agreement with the observational data. The departure of model and field data (diffusion plus advection) from a theoretical diffusion-alone situation (blue line in Figure 4) is the result of the advection velocity present in the snow.

4. Conclusions

[17] Air movement in snow and other porous media is complex and challenging to observe. We demonstrate the feasibility of an *in situ* measurement system using carbon monoxide (CO) as a transport tracer to study transport processes in natural porous media such as snow without gas extraction. An array of 28 sensors installed in the snow provided high temporal resolution data simultaneously at all locations. It was shown that the small, highly sensitive, inexpensive CO sensors performed well in snow when deployment includes careful *in situ* calibration.

[18] The application of an equivalent circuit model for the CO sensors employed allowed for sensor-specific calibration based on data obtained from as few as two *in situ* CO concentrations. Comparison of measurements and simulation results from a simple advection-diffusion model shows reasonable agreement, though inclusion of mechanical dispersion would be needed to better fit the data. The choice of CO has been shown to be a useful tracer for gas transport in snow and other relatively non-reactive porous media such as dry soil or sand.

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