Measurement of Gas Diffusion Coefficient in Highly Permeable Porous Media

Elad Levintal, Maria I. Dragila, Tamir Kamai, and Noam Weisbrod*

Gas diffusion is a fundamental transport process in porous media. However, to date, there is no method for experimentally estimating the gas diffusion coefficient of coarse porous media. A modified method is proposed here and was validated against sand media. The method was tested using particle sizes ranging between 1 and 4 cm:

\[ 10^{-3} \text{ cm}^2 < \text{intrinsic permeability} < 10^{-2} \text{ cm}^2. \]

Laboratory experiments were conducted in large horizontal columns filled with different homogeneous spherical particles inside a climate-controlled laboratory under isothermal (±<0.2°C) and windless conditions. Diffusion coefficients were similar for particles sizes of 1 and 2 cm, which indicates that pure diffusion governs gas transport. Above 2 cm, diffusion coefficients were higher, suggesting an enhanced gas transport, most likely initiated by small, local advective components. Because the enhanced transport can be modeled by the diffusion equation using a larger diffusion coefficient, it is associated with the enhanced diffusion concept.

Abbreviations: CCL, climate-controlled laboratory; PM, porous media; PS, particle size.

Accounting for gas fluxes within a porous media (PM), such as the upper vadose zone, requires partitioning the flux contribution from two transport mechanisms—diffusion and advection (Hamamoto et al., 2009a; Kuang et al., 2013; Nachshon and Weisbrod, 2015; Ben-Noah and Friedman, 2018). For purely Fickian diffusion, the key parameter comprising PM properties is the diffusion coefficient. Published models that are used to predict the gas diffusion coefficient \( D_p \) were developed from studies performed in PM of low and moderate intrinsic permeability, \( k \), hereafter called permeability (sand-sized particles and below, \( \sim 10^{-5} \text{ cm}^2 \)) (Bachmat and Bear, 1986; Scanlon et al., 2002; Resurreccion et al., 2008; Kühne et al., 2012). The lack of experimental tests performed in coarse PM leaves open the question if pure diffusion can be assumed to dominate transport in natural and artificial systems of high \( k \) even when ambient conditions that would drive advection are stable, within sensor resolution (i.e., no wind, thermal gradient, or pressure gradient conditions).

In the case of conservative species and zero pore-gas velocity (i.e., no advection and therefore no hydrodynamic dispersion), diffusion transport in PM is described by (Fujikawa and Miyazaki, 2005; Allaire et al., 2008)

\[ \frac{\partial C_g}{\partial t} = D_p \frac{\partial^2 C_g}{\partial x^2} \tag{[1]} \]

where \( \varepsilon (\text{cm}^3 \text{ cm}^{-3}) \) is the PM air-filled porosity, \( C_g (\text{g cm}^{-3}) \) is the gas concentration in the PM, \( t (s) \) is time, \( D_p (\text{cm}^2 \text{ air s}^{-1}) \) is the gas diffusion coefficient in the PM, and \( x (\text{cm}) \) is the coordinate in the direction of transport.

Models commonly use a relationship between the PM’s \( D_p \) and the free-air gas diffusion coefficient \( D_0 \) (Chamindu Deepagoda et al., 2011; Massman, 1998), \( D_p/D_0 \) known as the gas diffusivity or the relative diffusivity (e.g., Masis-Meléndez et al., 2014). The value of \( D_0 \) incorporates the effects of gas species and local temperature and pressure (Reid et al., 1987; Massman, 1998). Therefore, the ratio \( D_p/D_0 \) only accounts for the effect of the physical properties of the PM on transport (e.g., Buckingham, 1904; Thorbjørn et al.,...
including porosity, tortuosity, and pore size, that dictate the magnitude of viscous dissipation (Wu et al., 1998; Allaire et al., 2008). A number of models for diffusivity in PM have been proposed over the years; some of the most common are cited in Table 1. These models were developed based on data collected from relatively fine-textured PM (with low k), and here are tested for their validity with coarse-textured PM (with high k). In general, most of the models predict the diffusivity to be a function of the air-filled porosity, ε. An important parameter that changes with air-filled porosity is the tortuosity. The tortuosity is a complex property that expresses the mean path length through which the gas diffuses in the pore space. By lumping this complexity into a single tortuosity factor, it has been shown that this factor depends on moisture content and on the shape of the particles (size and structure) and their arrangement in the pack. However, for the case of dry coarse PM constructed from particles of the same shape, as in this study, the tortuosity factor is considered a function of ε only (Troeh et al., 1982; Thorbjørn et al., 2008). Therefore, by geometric similarity, the tortuosity of all four PMs in this study will be assumed to be constant, given the same ε.

Because coarse PM are common in natural and man-made processes, e.g., soil aggregates (Ganot et al., 2014) or the crushed rock layer used for thermal stabilization of railway/highway embankments in permafrost regions (Zhang et al., 2013), there is value in properly estimating $D_P/D_0$ for coarse PM as well and in identifying if diffusion as a mechanism is applicable in high k media. In high-permeability aggregated soils, gas transport drives various processes, including aeration of the root zone (Kawamoto et al., 2006), volatilization of organic chemicals (Aachib et al., 2004), and water vapor diffusion (e.g., Ross, 1984). In snow, Massman and Frank (2006) studied the effect of gas transport mechanisms on CO$_2$ fluxes emanating from snowpack. In waste rock generated from mining activity, O$_2$ transport from the atmosphere leads to oxidation of sulfide minerals that can lead to environmental risk (Amos et al., 2015, 2009). Consequently, it is essential to determine the limitation of diffusion models to ensure proper risk assessment of gas transport (Thorbjørn et al., 2008).

Table 1. Classical models for the prediction of relative diffusivity, $D_P/D_0$ (modified from Kristensen et al., 2010).

<table>
<thead>
<tr>
<th>Model</th>
<th>Originally developed for</th>
<th>Reference</th>
<th>$D_P/D_0$ (for ε = 0.45)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_P/D_0 \propto \varepsilon^2$</td>
<td>variable-textured natural soils</td>
<td>Buckingham (1904)</td>
<td>0.20</td>
</tr>
<tr>
<td>$D_P/D_0 = 0.66\varepsilon$</td>
<td>dry porous materials</td>
<td>Penman (1940)</td>
<td>0.30</td>
</tr>
<tr>
<td>$D_P/D_0 \approx 10^{-3}/f^2$</td>
<td>coarse and unstructured material with particles of uniform size</td>
<td>Millington and Quirk (1961)</td>
<td>0.34</td>
</tr>
<tr>
<td>$D_P/D_0 = 0.9\varepsilon^2$</td>
<td>aggregated silt loam</td>
<td>Campbell (1985)</td>
<td>0.14</td>
</tr>
<tr>
<td>$D_P/D_0 = \varepsilon^{1.5}(\varepsilon/f)$</td>
<td>unstructured natural soils</td>
<td>Moldrup et al. (2000)</td>
<td>0.30</td>
</tr>
</tbody>
</table>

† $\varepsilon$, air-filled porosity; $f$, total porous medium porosity; for dry conditions, $f = \varepsilon$.

The methods discussed by Allaire et al. (2008) may not be applicable for coarse PM. Using an injection chamber, as required in these methods, is suitable under the assumption of a well-mixed chamber, which is difficult to achieve in large-scale columns without using active mixing (Rolston and Moldrup, 2002). Active mixing, such as that achieved by an air-fan in a gas chamber located below highly permeable (coarse) PM can generate additional transport components, which will violate the fundamental assumptions that only diffusion occurs and that advection is negligible. Furthermore, the relatively large soil volume of coarse PM requires a larger experimental setup than those described by Allaire et al. (2008). Therefore, modification of the method is needed to quantify diffusive gas transport in coarse PM. Hamamoto et al. (2009b) presented the one-chamber method, in which the entire PM was saturated initially with N$_2$. Then the N$_2$ injection was stopped, allowing O$_2$ to enter into the PM only by diffusion. The change in O$_2$ at different column locations was then used to calculate $D_P$. Because their investigation was limited to sandy and loamy PM, the applicability of this method for high-permeability PM remains to be determined.

In this study, the Hamamoto and Currie methods were modified to quantify the diffusivity of gas in high-k media. The experiments were conducted under ideal diffusive conditions (potential advective sources were below the detection limit of the instrumentation). In addition to the coarse media, the proposed method was validated using homogeneous sand media with $k$ comparable to published studies.

Materials and Methods

Experiments using packed PM in large horizontal columns were conducted inside a climate-controlled laboratory (CCL) under isothermal and no-wind conditions. Each column was filled with identically sized spherical particles, testing a total of four particle sizes (1–4 cm). An additional column was used for validating the method, using packed sand and comparing the results to sand diffusion coefficients from Hamamoto et al. (2009b). For a tracer, CO$_2$–enriched air (0.2%) was used; the experimental procedure...
resembles the Currie method (Currie, 1960a, 1960b) and the one-chamber method (Hamamoto et al., 2009b), with modifications as detailed in the following.

**Climate-Controlled Laboratory and Column Configuration**

The set of experiments was conducted in an enclosed climate chamber, without (forced) air movement and under controlled isothermal conditions of 21 ± 1.9°C for the four spherical-shaped particle sizes (PSs) and 25 ± 0.8°C for the sand medium (for technical details, see Nachshon et al. [2011] and Ben Neriah et al., [2014]). The relatively coarse PM required a large experimental setup, with polyvinyl chloride columns 100 cm long and 30 cm in diameter. In each set of experiments, the column was packed vertically with a single uniform PS. The columns were closed at one end and open at the other. Overall, five homogeneous PM were used, each comprised of a unique and uniform PS: natural sieved silica sand within a diameter range of 0.08 to 0.15 cm and an effective size of 0.09 cm (i.e., diameter greater than that of 10% of the particle diameters) (1), and polystyrene spherical particles with diameters of 1, 2, 3, and 4 cm ± 6%, respectively (2–5). The ideal spherical shape of these particles enabled accurate \( k \) estimation. Additionally, these particles were noncompressible, impermeable, and made from nonreactive materials. Each column was packed in a similar manner by continuously filling while gently shaking the column, and \( \varepsilon \) was calculated as the ratio of the total void volume to the overall column volume. The void volume equalled the overall column volume minus the total particle volume. The total particle volume of the sand was calculated as the ratio between the total sand mass \((1.01 \times 10^3)\) g and the sand’s bulk density \((1.5 \text{ g cm}^{-3})\). For the other four PSs, the total particle volume was calculated by counting the number of particles in each column and multiplying by their volume. The volumes of the particles were evaluated by two different methods. In the first method, the diameter was measured with a caliper from a sample of each PS, and the particle volume was calculated from the average diameter value. In the second method, the particle volume was directly measured, using a known number of particles of each PS and immersing them in a known water volume inside a small column (volume of 1000 cm\(^3\)). The water volume after immersion divided by the number of particles inside the water gave the volume of each particle. Porosity estimate by the two methods differed by <2%. The \( k \) was estimated for each PS using the Kozeny–Carman equation, which gives satisfactory results for coarse media composed of uniform spherical particles (Nield and Bejan, 2013, p. 6; Levintal et al., 2017):

\[
\frac{k}{\mu} = \frac{180 \varepsilon^2 (1-\varepsilon)^3}{\left(\frac{d_p}{f}ight)^2}
\]

where \( k \) \((\text{cm}^2)\) is the permeability (i.e., intrinsic permeability), which is for dry media is directly related to the air permeability, \( d_p \) \((\text{cm})\) is the particle diameter, and \( f \) \((\text{cm}^3 \text{cm}^{-3})\) is the total PM porosity; under dry conditions, \( f = \varepsilon \). The columns’ properties are detailed in Table 2 (Columns A–C). After packing, the columns were oriented horizontally such that the side of the column was 40 cm above the CCL floor. The horizontal orientation ensured that even small perturbations in temperature that could move air by density gradients would not have as significant an effect as they would in a vertical orientation. A porous metal plate with holes of \(~0.5\) cm in diameter (total porosity of \(~0.5\)) was placed on the open side to hold the PM in the column and minimize particle relocations within it. The only exception was the sand column, which was not sensitive to temperature perturbations due to the relatively low \( k \) of the media (Levintal et al., 2017) and thus was oriented vertically.

For monitoring, the columns were instrumented with (Fig. 1): (i) 20 thermocouples (type T, Omega Engineering) inside the column at 5-cm intervals throughout the length of the column; (ii) four CO\(_2\) sensors (Vaisala GMD-20 CO\(_2\) transmitter), located at 20, 40, 60, and 80 cm from the open end of the column, and an additional sensor that was placed outside the column for measuring the ambient CO\(_2\) concentration, \([\text{CO}_2]\), inside the laboratory; and (iii) two differential-pressure sensors (1MBAR-D-4V, All Sensors Corp.) were located at distances of 20 and 80 cm from the open side of the column. These sensors were used for monitoring the

<table>
<thead>
<tr>
<th>Porous media properties</th>
<th>Fitting parameters</th>
<th>P0</th>
<th>P00</th>
<th>P000</th>
<th>P0000</th>
<th>P00000</th>
<th>P000000</th>
<th>P0000000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>Permeability ( k ) cm(^2)</td>
<td>Porosity ( \varepsilon ) cm(^3) cm(^{-3})</td>
<td>Fitted ( D_p ) cm(^2) s(^{-1})</td>
<td>Fitted ( D_p/D_0 )</td>
<td>Relative difference compared with 1-cm ( D_p/D_0 )</td>
<td>( R^2 )§</td>
<td>Bias§</td>
<td></td>
</tr>
<tr>
<td>0.09 (sand)</td>
<td>( 1.31 \times 10^{-4} )</td>
<td>0.44</td>
<td>4.0 \times 10^{-2} ± 0.7</td>
<td>0.249</td>
<td>83.1</td>
<td>0.990 ± 0.0</td>
<td>1.2 \times 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>( 1.56 \times 10^{-3} )</td>
<td>0.45</td>
<td>2.2 \times 10^{-2} ± 2.3</td>
<td>0.136</td>
<td>−</td>
<td>0.989 ± 0.6</td>
<td>−8.4 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( 6.48 \times 10^{-3} )</td>
<td>0.45</td>
<td>2.1 \times 10^{-2} ± 0.6</td>
<td>0.135</td>
<td>−0.8</td>
<td>0.986 ± 0.1</td>
<td>5.9 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( 1.46 \times 10^{-2} )</td>
<td>0.45</td>
<td>2.5 \times 10^{-2} ± 9.3</td>
<td>0.159</td>
<td>17.1</td>
<td>0.984 ± 0.2</td>
<td>2.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( 2.36 \times 10^{-2} )</td>
<td>0.45</td>
<td>3.0 \times 10^{-2} ± 6.4</td>
<td>0.188</td>
<td>38.1</td>
<td>0.978 ± 0.7</td>
<td>1.1 \times 10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

† All values are averaged from three repetitions, and the standard deviation represents the percent deviation from that average.
‡ \( D_p \) fitted to \([\text{CO}_2]\) data from the four sensors at distances of 20, 40, 60, and 80 cm.
§ \( R^2 \) and bias are the average of values from the four sensors. The \( R^2 \) standard deviation represents the percent deviation from the average of the three repetitions.
absolute pressure for assessing pressure buildup that might drive nondiffusive transport (1-Pa accuracy limit). Data from all sensors were logged at 10-min intervals (CR1000 datalogger, Campbell Scientific). For each CO₂ measurement, the sensors were activated for only 10 s to minimize sensor heating that might induce advective thermal disturbance. Preliminary experiments showed that activation of these sensors for longer times created heat that was significant enough to enhance gas transport. The experiments in this study were conducted under isobaric and isothermal conditions (i.e., no pressure or temperature gradients). We relax this statement to acknowledge the limitation of our measurement instrumentation, since pressure differences between the column and the ambient air could have existed but were necessarily below 1 Pa, which is the detection limit of the sensors installed within the column.

**Experimental Procedure**

The gas diffusion experiment was initiated with uniform [CO₂] within the column. To achieve this, prior to the experiment, the column was filled to saturation with air containing CO₂ tracer gas from an inlet located at the closed end of the column. Meanwhile, the open end of the column was covered to limit gas flux out of the column and enable a uniform [CO₂] distribution throughout the column. The open-end cover had a small open valve to minimize pressure increases inside the column. The inlet valve was then closed and the system was allowed to equilibrate for 60 s. To initiate the experiment, at time \( t_0 \), the open-end cover was gently removed; the initial [CO₂] throughout the column was 0.19 ± 0.01%. For \( t > t_0 \), [CO₂] in the column decreased toward the concentration in the CCL (i.e., atmospheric concentration: 0.0365 ± 0.0015%). Three repetitions were performed for each of the five PSs.

Two major modifications distinguish this method from the Currie method (Currie, 1960a, 1960b). First, the column size was much larger than that of Currie. The diameter of the column was 30 cm compared with only a few centimeters in the Currie method. The larger size, in both diameter and length, was adjusted to ensure that there were at least an order-of-magnitude ratio between the particle diameter and the column diameter and length (Lai and Kulacki, 1991). Another modification was the elimination of the source gas chamber, which for large \( k \) may have induced pressure gradients. In the Currie method, the source gas chamber required active mixing (e.g., an air fan), this could have potentially generated an advective transport component that we needed to suppress in our experiments. Whereas in the Currie method the experiment initiates with the PM being at ambient concentrations, letting the tracer gas diffuse into the column, in the proposed method the PM was initially saturated with the tracer gas, letting it diffuse out of the column into a large CCL that was at ambient concentration.

With respect to the one-chamber method suggested by Hamamoto et al. (2009b), the main modifications were: (i) the use of a larger experimental setup, with columns 100 cm long and 30 cm in diameter compared with 60 cm long and 5 cm in diameter; (ii) the use of larger 1- to 4-cm PSs compared with sandy and loamy PSs; and (iii) the use of CO₂–enriched air as a tracer, similar in its density to that of ambient air, rather than O₂ and N₂.

**Data Analysis**

To facilitate comparison between experiments with slightly different initial tracer concentrations (i.e., 0.19 ± 0.01%), the [CO₂] values were normalized to relative concentrations, \( C_r \):

\[
C_r = \frac{C - C_{atm}}{C_0 - C_{atm}}
\]

where \( C (\%) \) is the CO₂ gas concentration inside the column at a given location and time, \( C_0 (\%) \) is the initial [CO₂] (%) inside the column, and \( C_{atm} (\%) \) is the CCL ambient air [CO₂], which was assumed to be constant at 0.0365 ± 0.0015%.

**Estimating the Diffusion Coefficient**

Consider a homogeneous horizontal column of length \( l \), where gas transport is governed by one-dimensional diffusion in the \( x \) direction only (0 < \( x < l \)). The initial gas concentration in the column is \( C_0 \) and the column is exposed to the atmospheric concentration \( C_{atm} \) at one end \( (x = 0) \) and sealed at the other end \( (x = l) \), such that the initial and boundary conditions are
\[ C(x,0) = C_0; x \geq 0, \ t = 0 \]  
\[ C(0,t) = C_{atm}; x = 0, \ t > 0 \]  
\[ \frac{\partial}{\partial x} C(l,t) = 0; x = l, \ t \geq 0 \]

The latter boundary is achieved with the principle of superposition, using a \( C_{atm} \) at \( x = 2l \). Under these conditions, the solution for Eq. [1] is (Carslaw and Jaeger, 1959)

For estimating the diffusion coefficient of the PM, modeled concentrations (Eq. [5]) were fit to measured concentrations at specific distances (20, 40, 60, and 80 cm), optimizing for a unique \( D \) by minimizing the sum of least squares differences of modeled and measured concentrations from all locations simultaneously. The quality of the fits was statistically evaluated using the coefficient of determination \( (R^2) \). Evaluation of the model and the implementation of the least-squares optimization method were conducted with MATLAB (Version 9.2.0.538062), using built-in functions. The infinite sum in Eq. [5] was estimated by summing the first 100 terms (although beyond 10 terms there were minor differences), and the function \textit{lsqcurvefit} was used for the nonlinear optimization.

\[ C(x,t) = C_{atm} + \sum_{n=1}^{\infty} B_n \exp \left( -D \frac{n^2 \pi^2}{4l^2} t \right) \sin \left( \frac{n \pi x}{2l} \right) \]

where

\[ B_n = \frac{1}{l} (C_0 - C_{atm}) \int_0^{2l} \sin \left( \frac{n \pi x}{2l} \right) dx \]

and

\[ D = \frac{D_p}{\varepsilon} \]

\section*{Results and Discussion}

\subsection*{Multi-location Carbon Dioxide Analysis}

As expected, diffusion of gas led to a continuous decrease of [CO2] within the columns (Fig. 2). The results among repetitions were very similar (with related uncertainty analysis discussed below). For simplicity, figures present results for one repetition only for each PS. The relative gas concentration, \( C_r \), for each of the five PSs at each of the four locations within their respective columns is presented in Fig. 2. The corresponding fitting statistics are listed in Table 2. For each PS, the optimization gave a single and unique \( D \), from which a corresponding \( D_p \) was calculated (Eq. [5] and [7]).

The method presented here was validated using results from the sand experiment (Fig. 2a). The diffusion model (Eq. [5]) displayed good agreement with the data from the sand experiment \((R^2 = 0.990)\), with optimized \( D_p/D_0 = 0.249 \). Likewise, Hamamoto et al. (2009b) reported \( D_p/D_0 \sim 0.250 \) for Narita sand, which had a similar PS and \( \varepsilon \) to the sand used here. The difference between those \( D_p/D_0 \) values is <0.5%, showing that
for sand the diffusion coefficient can be evaluated reliably with this method.

For the four larger PSs, all of the fits to Eq. [5] displayed good agreement with the data, having high coefficients of determination \((R^2 \geq 0.978)\) and without considerable bias (Table 2, Columns G and H). The \(D_p\) values were similar for the PM comprised of 1- and 2-cm PSs \((k = 1.56 \times 10^{-3} \text{ and } 6.48 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}, \text{ respectively})\). For PSs of 3 and 4 cm, the \(D_p\) values were only slightly higher and still well fitted by the diffusion model (Table 2, Column D). The agreement between modeled and measured results for all four PSs and permeabilities (Fig. 2a–2d) suggests that gas transport in the system is governed by diffusion.

The entire set of \(D_p/D_0\) values that were evaluated fall within the range of \(D_p/D_0\) values calculated by the models presented in Table 1 (Fig. 3). Although this indicates that gas transport is governed by diffusion, a clear trend of increasing \(D_p/D_0\) values (Table 2, Column E) with increasing \(k\) is seen (Fig. 3) beyond a PS of 2 cm. Because \(k\) is the only parameter differing across PSs, the driving mechanism causing the observed increasing trend in relative diffusivity is sensitive to \(k\).

Penman (1940) reported \(D_p/D_0 = 0.319\) (using glass spheres with \(d_p = 0.3 \text{ cm and } \varepsilon = 0.40\)), and Currie (1960b) reported \(D_p/D_0 = 0.252\) (also using glass spheres, with \(d_p = 0.55 \text{ cm and } \varepsilon = 0.38\)). The diffusivity obtained for the larger PSs were consistently lower than for the sand, although within the range of values found in the literature for macroporous systems (e.g., Allaire et al., 2008; Kristensen et al., 2010).

To provide confidence in the mathematical method used and in the resulting diffusion coefficients, we conducted an uncertainty analysis. The analysis compared fitted diffusivity values obtained from the combined sensor data to separate fits of the data from each sensor location. This was repeated for each PS separately (Fig. 4). Results of this analysis highlight two things. First, when analyzing each individual location, the diffusion model is highly correlated to the experimental \(C_r\) data. Second, while there are small differences when comparing the \(D_p/D_0\) values evaluated separately with those obtained simultaneously using all four locations, the individual values bracket the combined values for each PS. For example, using the 4-cm PS, the fitted \(D_p/D_0\) values using only 20- and 80-cm data were 0.175 and 0.190, respectively, compared with the fitted \(D_p/D_0\) from all four sensors combined of 0.189.

For gas transport that is purely diffusive, the common models suggest that the diffusion coefficient of dry PM \((D_p)\) may be predicted with the \(\varepsilon\) of the media alone (Table 1). If that was the case here, we would expect very similar \(D_p/D_0\) values for the different sphere sizes (1–4-cm diameter) of the tested media because their \(\varepsilon\) is almost identical \((0.45 \pm 0.01)\). However, the observations show that \(D_p/D_0\) values vary in relation to PS, with increasing \(D_p/D_0\) values for larger PSs (Fig. 3). Another parameter that strongly influences gas diffusion rates is the tortuosity. However, in these experiments because of intentional geometric similarity among media, the tortuosity is similar across all PM used and therefore
is most likely not driving the change in the observed diffusion coefficient (for PSs 2–4 cm).

A possible mechanistic explanation for the elevated diffusion rates for PS > 2 cm is the presence of small advective components that may enhance gas transport rates. For lower $k$ (i.e., PS 1–2 cm), viscous resistance may successfully suppress small advective fluxes. However, as $k$ increases (PS > 2 cm), the decrease in viscous resistance may enable advective conditions to drive transport. Small eddies generated by undetectable, local temperature variability within the media will act to locally accelerate molecular motion. Small increases in the transport speed of similar magnitude as molecular diffusion would result in Eq. [5] yielding a higher diffusion coefficient. Augmentation of the mean free path length for a small percentage of the gas molecules results in the appearance of a fast $C_r$ decrease, which can be seen in the early data, especially for the two largest PSs, and is a characteristic of enhanced diffusion (Benson et al., 2001).

Because of the small variation between experiment repetitions (Table 2, Column D), we conclude that differences across PSs are real and consistent. To test the possibility of enhancement due to advection driven by temperature variability, we compared the $C_r$ decrease and the temperature distribution of the 4-cm PS column between a vertical and horizontal orientation (Fig. 5). As can be seen from the curves for the vertical case (Fig. 5a1), the four curves almost merge, indicating advective enhancement of transport. In the vertical orientation, advective transport may be affected by gravity, driven by thermal differences (Nield and Bejan, 2006). This is a type of free convection, which develops in response to air-density gradients (Levintal et al., 2017). Although a similar scale of temperature differences existed in both orientations (\(\sim 0.2^\circ C\); Fig. 5a2 and 5b2), this temperature variability in the horizontal column would drive local eddies, yielding enhanced diffusive transport rather than advective (buoyancy) transport (Fig. 3b1). This supports the observation of the increase in $D_p$ values for the 4-cm PS.

For the 1-cm-diameter PS, the $D_p$ and $R^2$ values were similar in both orientations, indicating that viscous dissipation was sufficient to suppress the low level of thermal advection. These results demonstrate the extreme sensitivity of the experimental system to temperature gradients. It is therefore emphasized that diffusion experiments in such highly permeable coarse PM should be performed in a horizontal orientation to minimize buoyancy effects.

Enhanced Diffusion

The diffusion coefficient for the PM with PS > 2 cm was found to be larger than those of 1-and 2-cm diameter but still within the predicted range suggested by the models (Fig. 3; Table 2). However, because of the observed trend with increasing $k$, we suggest relating this observation to enhanced diffusion. The concept of enhanced diffusion was previously reported with respect to wind-driven dispersive gas transport in snow (Bowling and Massman, 2011) and forest soil (Maier et al., 2012). Enhanced diffusion describes fluxes that are higher than molecular diffusion rates but are not advection dominated. In our case, this seems to be the situation; for PS > 2, we suggest there are internal advective components, but because these are of very small magnitude, similar to molecular diffusion rates, gas transport can be modeled as a diffusion-dominated system.

It is expected that field settings will pose less stable ambient conditions compared with the extremely stable CCL environment. Therefore, enhanced diffusion should be expected under natural
field settings of sufficiently high $k$ where pressure gradients from changes in barometric pressure (Sánchez-Cañete et al., 2013; Mourtzoukou et al., 2014) and winds (Takle et al., 2004; Laemmel et al., 2017) or temperature gradients (Ganot et al., 2014; Levintal et al., 2017) are commonly found. Within the experimental conditions, which were relatively very stable, $D_P/D_0$ increased by 39% as the PS changed from 2 to 4 cm (comparing average $D_P/D_0$ from three repetitions). However, all of the $D_P/D_0$ values were still within the range of theoretical diffusion model predicted values. The impact of this increase in $D_P/D_0$ on gas travel time is significant, as it considerably shortens the transport time. For instance, the calculated time for a 90% [CO$_2$] reduction at 60 cm from the atmospheric boundary is 199,260 s (55 h) for a PS of 2 cm with $k$ of $6.48 \times 10^{-3}$ cm$^2$/s compared with 142,260 s (39 h) in the 4-cm PS media with $k$ of $2.36 \times 10^{-2}$ cm$^2$/s. Thus, the potential enhancement of $D_P/D_0$ should be considered even under stable field conditions when evaluating gas transport in highly permeable PM.

### Summary and Conclusions

A modified method for evaluating the gas diffusion coefficient of highly permeable porous media was developed and tested. Large-scale column experiments were conducted under controlled laboratory conditions that maintained a quiescent atmosphere. Four different spherical particle sizes between 1- and 4-cm diameter, packed to similar porosity, were tested and data compared with different gas-diffusion models.

Values of the specific diffusivity, $D_P/D_0$, were similar for particle sizes of 1 and 2 cm but increased for 3 and 4 cm. This increase in $D_P/D_0$ values with increasing permeability is suggested to be caused by small and local advective components that occur even under highly stable environmental conditions of no wind and undetectable pressure gradients.

Although the diffusion coefficient increased for the two larger particle sizes, all of the data were highly correlated ($R^2 = 0.978$) with the diffusion transport model (Eq. [5]), and the resulting $D_P/D_0$ values were in the range of values predicted by common predictive models. Therefore, because the magnitude of the advective component of transport was on the order of molecular diffusion, we categorized the increase in gas transport as enhanced diffusion. Average $D_P/D_0$ results were $0.136 \pm 0.002, 0.135 \pm 0.001, 0.159 \pm 0.016$, and $0.188 \pm 0.012$ for PS diameters of 1, 2, 3, and 4 cm, respectively. These PSs have estimated permeabilities values of $1.56 \times 10^{-3}, 6.48 \times 10^{-3}, 1.46 \times 10^{-2}$, and $2.36 \times 10^{-2}$ cm$^2$, respectively.

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