Measuring diffusion using the differential form of Fick’s law and magnetic resonance imaging

C E Muir1, B J Lowry2 and B J Balcom1,3,4

1 Department of Chemistry, University of New Brunswick, PO Box 4400, Fredericton, NB, E3B 5A3, Canada
2 Department of Chemical Engineering, University of New Brunswick, PO Box 4400, Fredericton, NB, E3B 5A3, Canada
3 Department of Physics, University of New Brunswick, PO Box 4400, Fredericton, NB, E3B 5A3, Canada
E-mail: bjb@unb.ca

New Journal of Physics 13 (2011) 015005 (15pp)
Received 29 July 2010
Published 28 January 2011
Online at http://www.njp.org/
doi:10.1088/1367-2630/13/1/015005

Abstract. Diffusion is an important process in many biological and industrial processes. Diffusion coefficients are traditionally measured using integrated solutions of Fick’s law for systems with well-defined boundary conditions. We report a simple method for measuring diffusion coefficients in processes without well-defined boundary conditions or without a simple integrated solution using the differential form of Fick’s law. Magnetic resonance imaging (MRI) was used to obtain spatially and time-resolved profiles of the diffusion of H2O from an agarose gel to a neighboring D2O reservoir. The differential form of Fick’s second law was used to solve for the diffusion coefficient, \( D = 1.3 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \). MRI is well suited to this type of analysis as it naturally generates time- and space-resolved images. This analytical method allows for the determination of diffusion coefficients in systems that lack an integral solution to the diffusion equation.

4 Author to whom any correspondence should be addressed.
1. Introduction

Diffusion is a process common to many important porous media systems. The measurement of diffusion coefficients (diffusivity) is central to understanding diffusion processes that occur naturally in porous biological and chemical systems. Numerous techniques and instruments exist for the measurement of diffusivity. The diaphragm cell, the infinite couple and Taylor dispersion are some of the commonly used methods for measuring diffusion coefficients [1]. Nuclear magnetic resonance (NMR) offers benefits for measuring coefficients of self-diffusion, the movement of a tagged solute particle within a chemically identical solvent [1]. The NMR pulsed field gradient (PFG) method is non-invasive and no concentration difference between the two solutions is necessary for the determination of a diffusion coefficient [1].

Diffusive mass transfer in porous media is frequently measured in experiments where one controls or imposes well-known boundary conditions on samples and processes of interest. Ideal boundary conditions permit the integration of Fick’s law and fitting of either time or spatially varying concentration data to determine diffusion coefficients [2]–[5]. However, many practical mass transfer processes do not correspond to convenient boundary conditions and therefore have no integrated solution to Fick’s law. In other cases, an integrated solution to Fick’s law may exist but may be complex and challenging to fit in order to solve for the diffusion coefficient. In either of these situations an alternative approach to measuring the diffusion coefficient is through the differential form of Fick’s second law.

The usefulness of the differential approach has been demonstrated by Karger et al [6] in their recent study of the distribution of guest molecules in nanoporous host materials. Interference microscopy was used to generate concentration profiles and determine diffusivity, but the method was limited to optically transparent samples. Magnetic resonance imaging (MRI) is a non-invasive method that can be used to study both transparent and opaque samples. In this work, we use MRI to generate spatially and time-resolved profiles in which the measured signal is proportional to the concentration of H$_2$O. This naturally allows for easy use of the differential diffusion equation to determine the diffusion coefficient, $D$. 

References
2. Theoretical background

Diffusion can be described by Fick’s second law of diffusion in terms of concentration, \( C \), time, \( t \), and space, \( x \),

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},
\]

where \( D \) is the diffusion coefficient [2]. Knowing \( \partial C/\partial t \) and \( \partial^2 C/\partial x^2 \), one can easily solve for \( D \). In order to determine reliable values, it is necessary to smooth the concentration data [7, 8]. MRI is a powerful analytical technique but suffers from low intrinsic sensitivity. Without smoothing, the derivatives are unreliable due to a poor signal-to-noise ratio (SNR). The \( \partial C/\partial t \) and \( \partial^2 C/\partial x^2 \) values can be determined through differentiation with weighted differences and weighted differences of differences equations, respectively, as shown in (2)–(4) [8]. These equations are normalized incremental versions of Gasser’s optimal kernel (1,3) and (2,4) functions for continuous functions. The equations do not rely on additional smoothing because the smoothing is implicit in the method. A sample derivation of (2)–(4) is provided in appendix A. The time difference between two consecutive profiles is represented by \( \Delta t \). In this work, \( \Delta t = 360 \) s. The central concentration value is represented by \( C_i \), and \( \Delta x \) is the distance between two adjacent points on a profile. In this work, \( \Delta x = 6.59 \times 10^{-3} \) m.

\[
\frac{\partial C}{\partial t} = \frac{11}{140} (C_{i+1} - C_{i-1}) + \frac{16}{140} (C_{i+2} - C_{i-2}) + \frac{9}{140} (C_{i+3} - C_{i-3}) \quad \text{(2)}
\]

\[
\frac{\partial C}{\partial t} = \frac{29}{1342} (C_{i+1} - C_{i-1}) + \frac{52}{1342} (C_{i+2} - C_{i-2}) + \frac{63}{1342} (C_{i+3} - C_{i-3}) + \frac{56}{1342} (C_{i+4} - C_{i-4}) \quad \text{(3)}
\]

\[
\frac{\partial^2 C}{\partial x^2} = \frac{-150}{3861} C_i - \frac{121}{3861} (C_{i+1} + C_{i-1}) - \frac{44}{3861} (C_{i+2} + C_{i-2}) + \frac{51}{3861} (C_{i+3} + C_{i-3}) \quad \text{(4)}
\]

In this work, the concentration values, \( C \), are taken from the MRI profiles, where the measured signal is proportional to the H\(_2\)O concentration. The time and spatial values are naturally generated through MRI. The MRI method used in this work was single point ramped imaging with \( T_1 \) enhancement (SPRITE) [9]. SPRITE was chosen because it is a quantitative density imaging technique. The double half-\( k \)-space (DHK) method is one of a collection of centric-scan SPRITE techniques that sample the origin of \( k \)-space first such that no \( T_1 \) weighting is introduced at the \( k \)-space origin [10]. DHK SPRITE, figure 1, samples one half of \( k \)-space from 0 to \(+k\), waits for five times the relaxation time \( T_1 \) and then samples the other half of \( k \)-space from 0 to \(-k\).

The local image signal intensity, \( S \), is given by

\[
S = \rho \exp \left( \frac{-t_p}{T_2^*} \right) \sin \alpha,
\]

New Journal of Physics 13 (2011) 015005 (http://www.njp.org/)
Figure 1. 1D DHK SPRITE pulse sequence. One half of k-space is sampled and then after a delay of 5 × T₁, the second half of k-space is sampled. The RF pulse is applied at intervals of TR. A single point or multiple points from the free induction decay (FID) are collected after encoding time, t_p.

Figure 2. Schematic diagram illustrating the movement of H₂O from the 2% agarose gel to the D₂O reservoir. The D₂O reservoir was well mixed.

where ρ is the local proton density, t_p is the experimental encoding time, T₂* is the effective spin–spin relaxation time and α is the flip angle of the radio frequency (RF) pulse. It can be seen from (5) that when t_p ≪ T₂* and when α is constant over the field of view of the image, the signal is directly proportional to the concentration of ¹H, which in this work is equal to the concentration of H₂O.

3. Experimental

An agarose gel, 2%, was formed from a mixture of distilled water and agar powder. The solution was heated to boiling and then poured into a glass cylinder (6.8 cm in length, 3 cm in diameter), which was sealed at both ends with Teflon plugs (0.5 cm in length, 3 cm in diameter), as illustrated in figure 2. The gel was cooled passively to room temperature and then placed in a 2 mM solution of CuSO₄ for 48 h. The gel was removed from the CuSO₄ solution, cut to 3 cm with a razor blade and returned to the glass cylinder. A solution of 2 mM CuSO₄ in 99.9% D₂O was placed on top of the agarose gel. The sample remained horizontal for the duration of the measurements.
The one-dimensional (1D) profiles were obtained using a permanent magnet (8.3 MHz) with a 9.5 cm pole gap and a 20 cm long, 16 turn solenoid RF probe (4.8 cm i.d.) controlled from a Tecmag (Houston, TX) Apollo console. The gradient set was homebuilt [11] and water cooled, driven by Techron (Elkhart, IN) 7780 amplifiers.

The repetition time, TR, was set to 2 ms, and the encoding time, $t_p$, was set to 70 $\mu$s. The dwell time was set to 8 $\mu$s, and the gradient increment $\Delta G$ was set to 0.39 G cm$^{-1}$. A total of 128 points were acquired and the field of view was 8.7 cm. The $90^\circ$ pulse was 20.5 $\mu$s, and a pulsewidth of 3 $\mu$s ($\alpha = 13^\circ$) was used for the profile acquisition. A total of 32 averages were collected in 1 min.

Bulk $T_1$ measurements were carried out with an inversion recovery method. A total of 32 $\tau$ values were used, biased toward the earlier delays, and four scans were acquired with a delay of 1 s between scans. Bulk $T_2$ measurements were carried out with a Carr–Purcell–Meiboom–Gill (CPMG) sequence. A total of 16 scans were acquired with 512 echoes and a 200 $\mu$s echo time with a 1 s delay between scans. Bulk $T^*_2$ values were determined by fitting to the free induction decay.

1D profiles were collected at even time intervals ($\Delta t$) after the addition of D$_2$O to the agarose gel at 19°C. $\Delta t = 180$ s from $t = 0$ to 100 min, $\Delta t = 360$ s from $t = 100$ to 292 min and $\Delta t = 660$ s from $t = 292$ to 511 min.

4. Results and discussion

1D SPRITE DHK profiles were obtained from 0 to 511 min after the D$_2$O reservoir was placed adjacent to the agarose gel in the glass tube (figure 3). The signal intensity in the profiles is directly proportional to the H$_2$O concentration. By obtaining time-resolved profiles, we can observe the diffusion of H$_2$O from the agarose gel to the D$_2$O reservoir. It was assumed that the H$_2$O concentration is uniform across the vessel with no wall effects. Relaxation times will change as H$_2$O forms HDO when it comes in contact with D$_2$O. A simple set of measurements was carried out to demonstrate this fact. A pure H$_2$O solution had a measured $T_1 = 2.0$ s and $T_2 = 1.9$ s, while a 90% D$_2$O/10% H$_2$O solution had $T_1 = 4.8$ s and $T_2 = 4.1$ s at 15 MHz. The DHK SPRITE measurement is immune to such changes in $T_1$ and $T_2$ and therefore the profiles remain unaffected.

The smoothing and differentiation operations, (2)–(4), were used to obtain values for $\partial^2 C/\partial x^2$ and $\partial C/\partial t$. In the spatial direction, points along the profiles that experienced a significant change in concentration with position were analyzed. These points had concentrations that were approximately 5% different from their neighboring points. Points 71–77 (approximately 5.1–5.6 cm in figure 3) were used in the analysis. Other points along the spatial direction were not considered. Data from early times were discarded because their profiles were affected by geometric blurring due to the nature of the imaging experiment and not the diffusion of H$_2$O. Data from late times were discarded because the selected $\Delta t$ did not allow for a significant change in concentration to occur before the next measurement. Diffusion coefficients were determined for each of the seven spatial points at times $t = 127$ to 158 min. Two weighted differences equations were used on the concentration versus time data to obtain two different sets of diffusion coefficients. Equation (3) used five terms that allowed for more smoothing than (2), which used only three terms. The resulting diffusion coefficients from using (2) to determine $\partial C/\partial t$ are shown in the second column of table 1. Equation (3) provided similar but more accurate results due to more smoothing. The resulting diffusion coefficients
Table 1. H$_2$O diffusion coefficient values measured using Fick’s law.

| Time (min) | $D$(m$^2$s$^{-1}$)$^a$ | $D$(m$^2$s$^{-1}$)$^b$ |
|------------|-------------------------|-------------------------|
| 127        | $1.14 \times 10^{-9}$   | –                       |
| 133        | $8.75 \times 10^{-10}$  | –                       |
| 139        | $8.60 \times 10^{-10}$  | $1.16 \times 10^{-9}$   |
| 145        | $9.58 \times 10^{-10}$  | $1.15 \times 10^{-9}$   |
| 152        | $1.30 \times 10^{-9}$   | $1.27 \times 10^{-9}$   |
| 158        | $1.90 \times 10^{-9}$   | $1.78 \times 10^{-9}$   |
| Average    | $1.2 \times 10^{-9}$    | $1.3 \times 10^{-9}$    |

$^a$Evaluated using equations (2) and (4).

$^b$Evaluated using equations (3) and (4).

Figure 3. 1D SPRITE DHK profiles of diffusion of H$_2$O from the agarose gel to the D$_2$O reservoir. The agarose gel is on the right side of the image. Profiles obtained at 0 min (●), 6 min (○), 32 min (▼), 87 min (▽), 156 min (■), 336 min (□), 500 min (●) after the D$_2$O reservoir was placed adjacent to the agarose gel. The reservoir was well mixed. D$_2$O was used to isolate the $^1$H signal from the H$_2$O.

are shown in the third column of table 1. Equation (4) was used consistently for the $\partial^2 C/\partial x^2$ value. The data in table 1 show an increasing trend in the diffusion coefficient with time. This may be due to the inherent blurring of the imaging technique. However, the measured diffusion coefficients are still within the experimental error of the measurement, which is estimated to be 12% based on estimated uncertainties in the spatial and temporal directions.

A PFG spin echo NMR measurement [12] was employed to determine self-diffusion coefficients of H$_2$O at 19 °C. The temperature was maintained at 19 °C due to the water-cooled...
The PFG measurement employed a 90° pulse width of 23 μs, a 180° pulsewidth of 46 μs, a gradient application time, δ, of 3 ms and a diffusion time, Δ, of 105 ms. The echoes were collected over 16 gradient steps, with a maximum gradient of 10 G cm−1. The repetition time was set to 5 × 9.45 for each sample. Measurements were made in liquid H2O, a 50:50 D2O/H2O solution, and a 2% agarose gel. The solutions and gel were all doped with 2 mM CuSO4. The CuSO4 did not have an effect on the H2O diffusion coefficients. The resulting H2O self-diffusion coefficients were \( D_{\text{H2O}} = 2.17 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \), \( D_{\text{D2O/H2O}} = 1.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) and \( D_{\text{gel}} = 1.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \). These values are in close agreement with the literature values. The self-diffusion coefficients of pure H2O and D2O as reported by Mills were 15.87 × 10−9 m2 s−1 and 14.4 × 10−9 m2 s−1 at 25 °C [13]. Klemm et al [5] reported self-diffusion coefficients of \( D_{\text{H2O}} = 1.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) and \( D_{\text{D2O}} = 1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) at 20 °C, where the H2O and D2O had a gel content of 1.2%.

Our diffusion experiment contained both a gel and a D2O reservoir. We would expect the \( D \) values obtained from our interdiffusion experiment to be less than the \( D \) found through the PFG measurements for H2O self-diffusion in a gel and in an H2O/D2O mixture. H2O diffusion in the gel is expected to give rise to a lower diffusion coefficient than self-diffusion in liquid H2O because the gel contains a network structure that hinders diffusion. D2O has a higher molecular weight than H2O and therefore a larger moment of inertia, resulting in a lower diffusion coefficient [14]. The diffusion of H2O is slowed down in the presence of D2O because the H2O can only move into space vacated by the D2O. HDO will form in the presence of H2O/D2O, but not by chemical proton exchange [15]. Diffusion is a coupled process. Therefore, H2O can only move into space vacated by the slower moving D2O molecules. The average \( D \)-value obtained from the third column of table 1 is 1.3 × 10−9 m2 s−1, which agrees with the expected outcome.

The results from the differential form of Fick’s law were compared with an integrated solution, shown in (6)–(8), where \( C_0 \) is the initial concentration of H2O in the gel, \( L_1 \) is the length of the D2O reservoir and \( L_2 \) is the length of the H2O gel. The detailed solution is provided in appendix B. It is clearly a less desirable, complicated diffusion case. The solution is based on 1D unsteady diffusion from a gel to a well-mixed reservoir. The D2O reservoir was well mixed due to passive convection and sample vibration induced by the vibration of the gradients.

\[
C(x, t) = C_0 \left[ \frac{L_1}{L_1 + L_2} + \sum_{n=1}^{\infty} \hat{B}_n \cos \left( \frac{\beta_n x}{L_1} \right) e^{-\beta_n^2 D t / L_1^2} \right],
\]

\[
\hat{B}_n = \frac{2 L_1 \sin \beta_n}{(L_1 + L_2 \cos^2 \beta_n) \beta_n},
\]

\[
\beta \cot \beta = -\frac{L_1}{L_2}.
\]

It is evident from (6)–(8) that the integrated solution for the current diffusion problem is complicated and fitting to the equation would be challenging. The raw data from profiles within the time range for optimal diffusion were plotted along with (6) with a \( D \) value that provided a close match of the experimental curves. An example is illustrated in figure 4. A diffusion coefficient value of \( \sim 2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) allowed for curves with the most overlap with the experimental data; however, this value is too high based on the self-diffusion data. The differential form of Fick’s law provides a more reliable answer.
Figure 4. Comparison of experimental data at 139 min (□) and an integrated solution curve with $D = 2.5 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ (solid line). The horizontal axis is the position over the length of the agarose gel. The vertical axis is the normalized signal intensity.

5. Conclusion

MRI and the differential form of Fick’s law have been used to determine the diffusion coefficient of H$_2$O in an H$_2$O agarose gel with an adjacent D$_2$O reservoir, $D = 1.3 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. The technique is a simple alternative to a complicated integrated form of Fick’s law. It provides accurate diffusion coefficient values. The method could be extended to various diffusion cases where the boundary conditions are not well defined or the diffusion equation does not have a simple integrated solution. If the diffusion problem is not a 1D problem, then one could apply the same methodologies but with slice selection of a 1D portion of the sample. Alternately, one could simply undertake the imaging in 2D or 3D. MRI is well suited to such analyses because it naturally generates spatially and time-resolved images.

Acknowledgments

CEM thanks NSERC of Canada for financial assistance (PGS D). BJB thanks NSERC of Canada for a Discovery Grant and the Canada Chairs program for a Research Chair on MRI of materials. The MRI Centre is supported by an NSERC Major Resources Support grant. BJL thanks NSERC and the Canadian Space Agency for support.

Appendix A. Sample derivation of differential and smoothing equations

A.1. Derivation of $\partial C / \partial t$ with three terms (equation (2) in this paper)

First, scale $k_{2,\text{norm}}(x)$ from Gasser et al [8] to a window with width $\lambda = (b + (1/2)) \Delta x \rightarrow k_2(x)$. Then, integrate over the increment $\Delta x$, centered around
\[ x_i = x + i\Delta x \rightarrow \hat{k}_2(x), \]
\[ \bar{y}_i'' = \sum_{j=-b}^{b} \hat{k}_2(j\Delta x)y_{i+j}\Delta x, \]
\[ b = 3, \quad \lambda = 7/2, \]
\[ \hat{k}_1(x) = \frac{15x}{4\lambda^3} \left[ 1 - \frac{(\Delta x)^2}{4\lambda^2} \right] - \frac{15x^3}{4\lambda^5}. \]

When \( \Delta x = 1 \):
\[ \hat{k}_1(1) = \frac{1320}{16\,807}, \quad \hat{k}_1(2) = \frac{1920}{16\,807}, \quad \hat{k}_1(3) = \frac{1080}{16\,807}. \]

The equation obtained from integrating Gasser’s kernel functions is
\[ \bar{y}_i'' = \frac{1}{\Delta x} \left[ \frac{1320}{16\,807} (y_{i+1} - y_{i-1}) + \frac{1920}{16\,807} (y_{i+2} - y_{i-2}) + \frac{1080}{16\,807} (y_{i+3} - y_{i-3}) \right]. \]

Apply to \( y = x \):
\[ \bar{y}_i'' = \frac{1}{\Delta x} \left[ \frac{1320}{16\,807} (2\Delta x) + \frac{1920}{16\,807} (4\Delta x) + \frac{1080}{16\,807} (6\Delta x) \right] \]
\[ = \frac{16\,800}{16\,807}. \]

Hence, multiply the original formula by \( \frac{16\,807}{16\,800} \):
\[ \bar{y}_i'' = \frac{1}{\Delta x} \left[ \frac{11}{140} (y_{i+1} - y_{i-1}) + \frac{16}{140} (y_{i+2} - y_{i-2}) + \frac{9}{140} (y_{i+3} - y_{i-3}) \right]. \]

**Appendix B. Integral solution to Fick’s second law for diffusion from a gel to a well-mixed reservoir**

Diffusion takes place from a gel to a well-mixed reservoir. The system is 1D, but unsteady. The gel initially contains solute at some concentration \( C_0 \), but the solute diffuses out into
the reservoir, increasing the concentration in the reservoir from zero. The concentration is
continuous at the interface between the gel and the reservoir. At any given time, the overall
mass balance gives the concentration in the reservoir in terms of the concentrations across the
gel [16, 17]:
\[ \int_0^{L_1} C_1(z, t) \, dz + C_2(t) L_2 = C_0 L_1. \]
The concentration in the gel is therefore defined by a partial differential equation (PDE)
\[ \frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial z^2}, \]
and a corresponding initial condition and two boundary conditions:
\[ C_1(z, 0) = C_0, \]
\[ \left. \frac{\partial C_1}{\partial z} \right|_{z=0} = 0, \]
\[ C_1(L_1, t) = \frac{1}{L_2} \left( C_0 L_1 - \int_0^{L_1} C_1(z, t) \, dz \right). \]
Unfortunately, integral boundary conditions are not tractable in separation of variables. It is
necessary to define an integral parameter here, in order to proceed:
\[ m(z, t) = \int_0^z C_1(u, t) \, du. \]
The inverse relationship between the cumulative mass and concentration is simply
\[ C_1(z, t) = \frac{\partial m}{\partial z}, \]
which allows the original PDE to be converted from concentration into cumulative mass, by first
taking the derivative in terms of \( z \)
\[ \frac{\partial^2 C_1}{\partial t \partial z} = D \frac{\partial^3 C_1}{\partial z^3} \Rightarrow \frac{\partial m}{\partial t} = D \frac{\partial^2 m}{\partial z^2}. \]
The initial condition and two boundary conditions then become
\[ m(z, 0) = C_0 z, \]
\[ m(0, t) = 0, \]
\[ \left. \frac{\partial m}{\partial z} \right|_{z=L_1} = \frac{1}{L_2} \left[ C_0 L_1 - m(L_1, t) \right]. \]
Separation of variables is simplest if the cumulative mass is broken into a steady solution with
the above boundary conditions (the last two conditions), and an unsteady solution with an initial
condition and two homogeneous boundary conditions:
\[ m(z, t) = m_s(z) + m_u(z, t). \]
The PDEs for each part of the cumulative mass are

\[
\frac{\partial^2 m_s}{\partial z^2} = 0,
\]

\[
\frac{\partial m_u}{\partial t} = D \frac{\partial^2 m_u}{\partial z^2}.
\]

The boundary condition that was initially zero remains zero in both cases,

\[ m_s(0) = m_u(0, t) = 0, \]

while the derivative boundary condition becomes

\[
\left. \frac{\partial m_s}{\partial z} \right|_{z=L_1} = \frac{1}{L_2} \left[ C_0 L_1 - m_s(L_1, t) \right],
\]

\[
\left. \frac{\partial m_u}{\partial z} \right|_{z=L_1} = -\frac{1}{L_2} m_u(L_1, t).
\]

The solution for the steady cumulative mass is a linear profile,

\[ m_s(z) = a z + b, \]

where the coefficient \( b \) is eliminated by applying one boundary condition,

\[ m_s(0, t) = 0 \Rightarrow b = 0, \]

while \( a \) is determined from the other boundary condition,

\[
\left. \frac{\partial m_s}{\partial z} \right|_{z=L_1} = \frac{1}{L_2} \left[ C_0 L_1 - a L_1 \right] \Rightarrow a = \frac{L_1}{L_1 + L_2} C_0.
\]

The steady solution also determines the initial condition for the unsteady part

\[ m(z, 0) = C_0 z \Rightarrow m_u(z, 0) = C_0 z - a z = (C_0 - a) z = \frac{L_2}{L_1 + L_2} C_0 z. \]

Separation of variables must be used to solve for the unsteady part. The cumulative mass breaks into the product of two functions as

\[ m_u(z, t) \to f(z) \phi(t), \]

and the two boundary conditions become

\[ m_u(0, t) = 0 \Rightarrow f(0) = 0, \]

\[
\left. \frac{\partial m_u}{\partial z} \right|_{z=L_1} = -\frac{1}{L_2} m_u(L_1, t) \Rightarrow f'(L_1) = -\frac{1}{L_2} f(L_1).
\]

The PDE then becomes

\[
\frac{\partial m_u}{\partial t} = D \frac{\partial^2 m_u}{\partial z^2} \to \frac{1}{D} \frac{\phi'(t)}{\phi(t)} = \frac{f''(z)}{f(z)} = -\lambda^2,
\]
so that the solutions for the two functions are
\[
\phi(t) = e^{-\lambda^2 D t},
\]
\[
f(z) = A \cos(\lambda z) + B \sin(\lambda z),
\]
where the time-varying function has been normalized to unity at zero time, in order to match the initial condition simply later on. The boundary conditions eliminate one constant,
\[
f(0) = 0 \Rightarrow A = 0,
\]
and the other boundary condition gives an implicit equation for the eigenvalue \( \lambda \):
\[
f'(L_1) = -\frac{1}{L_2} f(L_1) \Rightarrow B \lambda \cos(\lambda L_1) = -\frac{1}{L_2} \sin(\lambda L_1).
\]
This equation is most simply solved in dimensionless form, in terms of a parameter \( \beta = \lambda L_1 
\]
\[
\beta \cot \beta = -\frac{L_1}{L_2}.
\]
The solutions for the dimensionless parameter \( \beta \) give an infinite set of solutions, which can be computed numerically for any given geometry. For example, the solutions for the two cases \( L_1 = L_2 \) and \( L_1 = 0.5L_2 \) are tabulated below up to the fourth smallest value:

For \( L_1 = L_2 \):
\[
\beta_1 = 2.02875784, \quad \beta_2 = 4.91318044,
\]
\[
\beta_3 = 7.97866571, \quad \beta_4 = 11.08553841, \quad \ldots
\]

For \( L_1 = 0.5L_2 \):
\[
\beta_1 = 1.83659720, \quad \beta_2 = 4.81584232,
\]
\[
\beta_3 = 7.91705268, \quad \beta_4 = 11.04082982, \quad \ldots
\]
Once the dimensionless parameter is known it is easily substituted back into the solutions for the two functions, as
\[
\lambda_n = \frac{\beta_n}{L_1}.
\]
In these terms, the overall solution is therefore
\[
m(z, t) = a z + \sum_{n=1}^{\infty} B_n \sin \left( \frac{\beta_n z}{L_1} \right) e^{-\beta_n^2 (Dt/L_1^2)},
\]
where the Fourier coefficients can be found from the initial condition as
\[
B_n = \frac{\int_0^{L_1} (L_2/L_1 + L_2) \cdot C_0 z \sin (\beta_n (z/L_1)) \, dz}{\int_0^{L_1} \sin^2 (\beta_n (z/L_1)) \, dz} = C_0 \frac{2L_1^2 \sin \beta_n}{(L_1 + L_2 \cos^2 \beta_n) \beta_n^2}.
\]
Concentration is recovered from the cumulative mass by differentiating

\[ C_1(z, t) = \frac{\partial m}{\partial z} = a + \sum_{n=1}^{\infty} B_n \left( \frac{\beta_n}{L_1} \right) \cos \left( \frac{\beta_n z}{L_1} \right) e^{-\beta_n^2 \left( \frac{D t}{L_1^2} \right)} \]

\[ = C_0 \left[ \frac{L_1}{L_1 + L_2} + \sum_{n=1}^{\infty} \hat{B}_n \left( \frac{\beta_n}{L_1} \right) \cos \left( \frac{\beta_n z}{L_1} \right) e^{-\beta_n^2 \left( \frac{D t}{L_1^2} \right)} \right] , \]

where it is again convenient to work in terms of a dimensionless parameter

\[ \hat{B}_n = \frac{2L_1 \sin \beta_n}{(L_1 + L_2 \cos^2 \beta_n)} \beta_n . \]

This second parameter can also be tabulated, again using the two example cases \( L_1 = L_2 \) and \( L_1 = 0.5L_2 \) up to the fourth smallest eigenvalue:

\[ L_1 = L_2 : \hat{B}_1 = 0.739 659 49, \quad \hat{B}_2 = -0.383 629 77, \]

\[ \hat{B}_3 = 0.244 934 45, \quad \hat{B}_4 = -0.178 246 87, \ldots \]

\[ L_1 = 0.5L_2 : \hat{B}_1 = 0.923 308 37, \quad \hat{B}_2 = -0.404 449 13, \]

\[ \hat{B}_3 = 0.250 129 60, \quad \hat{B}_4 = -0.180 222 63, \ldots \]

Concentration in the reservoir follows from the cumulative mass at the interface as

\[ C_2(t) = C_1(L_1, t) = \frac{1}{L_2} \left( C_0 L_1 - \int_{0}^{L_1} C_1(z, t) \, dz \right) = \frac{1}{L_2} \left( C_0 L_1 - m(L_1, t) \right) , \]

so that

\[ C_2(t) = \frac{1}{L_2} \left( C_0 L_1 - aL_1 - \sum_{n=1}^{\infty} B_n \sin \beta_n e^{-\beta_n^2 \left( \frac{D t}{L_1^2} \right)} \right) \]

\[ = C_0 \left( \frac{L_1}{L_1 + L_2} - \frac{L_1}{L_2} \sum_{n=1}^{\infty} \hat{B}_n \beta_n \frac{L_1}{L_2} \sin \beta_n e^{-\beta_n^2 \left( \frac{D t}{L_1^2} \right)} \right) . \]

The concentration profiles are plotted on the following pages for the two example cases, but it is not possible to construct a general plot here, due to the dependence on the ratio of the gel length to the reservoir length. However, as is clear from the above example solutions, the higher modes of the solution, which decay fastest, are largely independent of the overall split between the gel and reservoir (note the similarity between the values for the fourth mode, for both parameters). This reflects that the concentration profile near the interface is independent of the influence of the lengths of the gel and reservoir—the higher order modes are effectively those with the shortest spatial influence.
References

[1] Cussler E L 2002 *Diffusion, Mass Transfer in Fluid Systems* 2nd edn (Cambridge: Cambridge University Press)
[2] Crank J 1993 *The Mathematics of Diffusion* 2nd edn (Oxford: Oxford Science)
[3] Balcom B J, Fischer A E, Carpenter T A and Hall L D 1993 *J. Am. Chem. Soc.* **115** 3300–5
[4] Balcom B J, Lees T J, Sharp A R, Kulkarni N S and Wagner G S 1995 *Phys. Med. Biol.* **40** 1665–76

*New Journal of Physics* **13** (2011) 015005 (http://www.njp.org/)
[5] Klemm A, Metzler R and Kimmich R 2002 Phys. Rev. E 65 021112
[6] Kärger J, Kortunov P, Vasekakov S, Heinke L, Shah D B, Rakoczy R A, Traa Y and Weitkamp J 2006 Angew. Chem. Int. Ed. Engl. 45 7846–9
[7] Lowry B J 1996 J. Colloid Interface Sci. 178 284–97
[8] Gasser T, Müller H-G and Mammitzsch V 1985 J. R. Stat. Soc. B 47 238–52
[9] Balcom B J, MacGregor R P, Beyea S D, Green D P, Armstrong R L and Brenner T W 1996 J. Magn. Reson. A 123 131–4
[10] Deka K, MacMillan M B, Ouriadov A V, Mastikhin I V, Young J J, Glover P M, Ziegler G R and Balcom B J 2006 J. Magn. Reson. 178 25–32
[11] Xia Y, Jeffrey K R and Callaghan P T 1992 Magn. Reson. Imaging 10 411–26
[12] Stejskal E O and Tanner J E 1965 J. Chem. Phys. 42 288–92
[13] Mills R 1973 J. Phys. Chem. 77 685–8
[14] Mills R and Harris K R 1976 Chem. Soc. Rev. 5 215–31
[15] Vinogradov S N and Linnell R H 1971 Hydrogen Bonding (New York: Van Nostrand-Reinhold)
[16] Haberman R 2004 Applied Partial Differential Equations: With Fourier Series and Boundary Value Problems 4th edn (Upper Saddle River, NJ: Pearson Education)
[17] Bird R B 2007 Transport Phenomenon 2nd edn (New York: Wiley)