

Evaluation of Laboratory Techniques for Measuring Diffusion Coefficients in Sediments

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■ Solute diffusion in freshwater sediments of Lake Okeechobee was analyzed by a technique whereby diffusion of a tracer (tritium) into the sediment was monitored from an overlying water column spiked with the tracer (method 1). Molecular diffusion coefficients (D_s) measured by this method were then compared with results from two other methods where solute diffuses from a spiked sediment column into an overlying water column (method 2) or solute diffuses from a spiked sediment column to a tracer-free sediment column (method 3). Method 1 yielded similar estimates of D_s compared to methods 2 and 3, as well as being a more efficient and less time-consuming procedure. Estimates of D_s from method 3, however, were lower than those for the other two methods, suggesting that the concentration profiles can be subject to more error during sediment extrusion and sectioning. Method 1, therefore, is ideally suited for laboratory estimates of D_s on packed or undisturbed sediment cores and, more importantly, lends itself to in situ measurement of solute diffusion in lake sediments.

Introduction

Biogeochemical processes in marine or freshwater sediments can produce large solute concentration gradients between the interstitial waters of sediment and overlying water. Concentration gradients between the overlying water and the sediment porewater can also develop as a consequence of added contaminants or nutrient inputs to the overlying water. These solutes are then subject to transport across the sediment-water interface via molecular diffusion, advection, and mixing processes caused by physical or biological activity.

Diagenetic models examine the total sum of changes, whether physical, chemical, or mineralogical, that occurs in sediments during and after their deposition. These models consider the mixing processes in terms of an effective diffusion coefficient (D_e ; units of L^2T^{-1}) as follows:

$$D_e = D_s + D_b + D_i + D_{wc} \quad (1)$$

where D_s is the molecular diffusion coefficient, D_b is the biodiffusion coefficient as a result of particle mixing, D_i is the irrigation coefficient due to the activity of benthic organisms, and D_{wc} is the wave and current mixing coefficient (1, 2). In sediment porewater, solute transport as a result of D_b , D_i , and D_{wc} may be similar in effect to D_s but not in mechanisms (i.e., flux not proportional to concentration gradient) (2, 3). In deep-sea sediments, coefficients for D_b , D_i , and D_{wc} are generally smaller than D_s ; however, in shallow, organic-rich sediments, D_i and D_{wc} values can be much greater than those for either D_b or D_s (1, 4). Below the zone of physical or biological disturbance, however, D_s is the dominant transport process (5). Therefore, molecular diffusion is an important process in the exchange of solutes or pollutants between the sediment-water interface.

Diffusion coefficients have generally been measured by a so-called "half-cell" technique, where two diffusion cells containing a porous medium are employed and one of the two half-cells is spiked with the solute of interest and joined to a nonspiked half-cell (6-8). After a specified period, the half-cells are separated and sectioned and the solute concentration in each increment is analyzed. The concentration profile thus determined is used to estimate D_s . Variations of this method include joining a spiked half-cell filled with a porous medium to another cell containing a water column (9, 10).

An alternative method to calculate diffusion coefficients without experimentation includes correcting free solution diffusion coefficients for the effect of sediment structure or tortuosity (11). Sediment tortuosity has been determined by estimating the electrical resistivity of the sediment or the formation resistivity factor (10). Formation resistivity factors have also been empirically determined from sediment porosities (11-13).

Although various laboratory methods have been developed for measuring D_s in interstitial waters of sediments, these methods are still very difficult and time-consuming. Hence, a more efficient and versatile method would be desirable. The purpose of this study, therefore, was (1) to estimate diffusion coefficients of a conservative, nonadsorbed tracer (tritiated water) in the laboratory, using the reservoir method, and (2) to evaluate the accuracy and versatility of the reservoir method with other techniques for measuring diffusion coefficients.

Materials and Methods

Littoral sediment samples collected from Lake Okeechobee in South Florida were used for measuring tritium diffusion coefficients employing three methods: reservoir to sediment diffusion (method 1), sediment to reservoir diffusion (method 2), and sediment to sediment diffusion (method 3). Method 1 has also been cited as the reservoir method (14), but for simplicity, the techniques will be referred to by their method number. A bulk sample of the sandy sediment was collected for methods 1 and 3 and intact cores of the littoral sediment were used for method 2. Schematic representation of these methods is presented in Figure 1.

Method 1. Reservoir to Sediment Diffusion. Two approaches were taken in method 1 to measure tritium diffusion coefficients: in method 1a changes in solute concentration in the reservoir were measured, whereas method 1b examined the tritium concentration profiles in the sediment cores upon the completion of method 1a.

Method 1a is described as follows. Four (cores L1-L4) Plexiglass tubes (3.2 cm in diameter, 8 cm long) were sealed to Plexiglass end plates with vacuum grease (Figure 1A), and saturated littoral sediment was packed into each column to a height of approximately 8 cm and allowed to settle for 48 h. Excess water was then removed from the surface, and one Whatman glass microfiber paper was placed on top of the sediment in order to minimize surface disturbance during water addition. The microfiber paper

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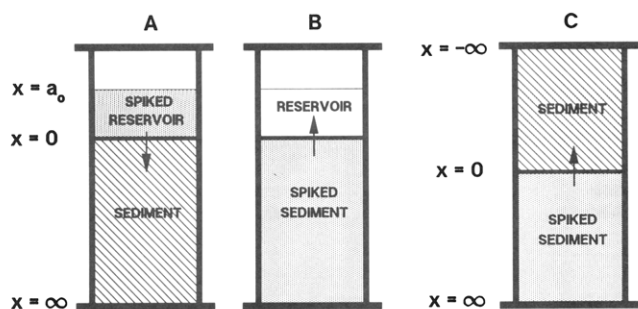


Figure 1. Experimental apparatus for measuring diffusion coefficients. (A) Reservoir to sediment diffusion (method 1); (B) sediment to reservoir diffusion (method 2); and (C) sediment to sediment diffusion (method 3).

was of sufficiently small diameter so as not to inhibit the diffusion process between the overlying reservoir solution and the sediment column. Another 8-cm-long Plexiglass cell was sealed on top of each of the cells filled with sediment and 10 mL of filtered lake water, spiked with the tritium tracer ($0.032 \mu\text{Ci}$), was added to each of the columns. Samples ($50 \mu\text{L}$) were then taken periodically from the reservoir over a period of 2 days. The reservoir was not stirred during sampling. The volume of solution in the reservoir was assumed to be constant, since less than 5% of the total reservoir solution was removed during sampling. Lids were placed on top of the columns to prevent evaporative losses of the reservoir solution.

Activities of tritiated water were measured on a Searle Analytic (Delta 300) liquid scintillation counter, using 5 mL of Scintiverse cocktail (Fisher Scientific Products) and a count time of 2 min. Relative concentrations (C_r/C_0) were calculated by using sample activities from the reservoir (C_r ; cpm mL^{-1}) and the initial activity of the tracer solution (C_0 ; cpm mL^{-1}). Upon completion of method 1a, cores L3 and L4 were set aside for later use in method 3.

At the end of the sampling period, the reservoir solution was removed and two sediment columns (L1 and L2) were extruded and sectioned at 1-cm increments, beginning at the bottom of the column (method 1b). This method ensured that the lower depths of the sediment did not become contaminated with tritium during extrusion. Tracer solutions were extracted from the sediment segments as follows. The sediment was placed in a 7-mL polycarbonate centrifuge tube that was perforated on the bottom and plugged with glass wool. This smaller tube, designed with an overhanging lip, was placed in a 35-mL tube for centrifuging at 200g. Activities of tritium from the sediment (C_s) were analyzed as described previously and the data reported as C_s/C_0 .

Volumetric water contents (θ) for the sediments were determined on the basis of weight differences between oven-dry (dried at 105°C) and saturated samples by use of smaller, packed columns without tracer.

Method 2. Sediment to Reservoir Diffusion. Briefly, method 2 is the reverse of method 1a, whereby tritium in a spiked sediment column diffuses into an overlying nonspiked reservoir solution (Figure 1B).

Three undisturbed samples, cores L5–L7 (4.4 cm in diameter and 20 cm long) were collected from the littoral zone of Lake Okeechobee, sealed, and transported to the laboratory. Method 1a was first utilized on these cores to calculate D_s ; however, the volume of the tracer solution was 20 mL. After the experiment was completed, the reservoir solution was left intact for 1 month in order to ensure a uniform concentration of tritium in the sediment column. A 30-mL aliquot of filtered lake water was then replaced on top of the spiked half-cell, and $50\text{-}\mu\text{L}$ samples

were taken periodically over a 2-day period from the reservoir and analyzed for tritium as described above.

Method 3. Sediment to Sediment Diffusion. The sediment–sediment system consisted of two Plexiglass half-cells, with each cell being 8 cm long with a surface area of 7.6 cm^2 (Figure 1C). Columns L3 and L4 from method 1a were used as the spiked half-cells for this study. The spiked and nonspiked half-cells were then held together with metal rods fastened through the end plates. The two cells were separated by one piece of Whatman glass microfibre paper. After 2 days, the cells were separated and sectioned into 1-cm increments. The increments were centrifuged and analyzed for tritium as described in method 1b to yield a tritium concentration profile.

Theory

The governing equation for diffusive transport between a liquid reservoir and a saturated porous medium such as sediment, based on Fick's second law, is as follows:

$$\frac{\partial C_r}{\partial t} = \frac{D_s}{R} \frac{\partial^2 C_s}{\partial x^2} \quad (2)$$

where C_r is the solute concentration in the reservoir (ML^{-3}), C_s is the solute concentration in the porewater (ML^{-3}), C_0 is the initial concentration (ML^{-3}) in the reservoir, D_s is the molecular diffusion coefficient (L^2T^{-1}), R is the retardation factor (dimensionless), x is distance (L), and t is time (T).

The retardation factor, R , is defined as

$$R = 1 + \rho K_d / \theta \quad (3)$$

where ρ is the sediment bulk density (ML^{-3}), θ is the volumetric water content (L^3L^{-3}), and K_d is the sorption coefficient for a linear isotherm (L^3M^{-1}). For a conservative, nonreactive tracer K_d is 0 and hence $R = 1$. For most soils (except those high in oxides) tritium has been shown to be a conservative, nonreactive tracer.

The molecular diffusion coefficient, D_s , can be related to the diffusion coefficient in bulk solution, D_0 (L^2T^{-1}), by (15)

$$D_s = D_0 \tau \quad (4)$$

where τ is the tortuosity factor (L^2L^{-2}), which accounts for the tortuous pathways in the sediment pore sequences. Typical values of τ range from 0.2 to 0.6 for soils (16), and from 0.5 to 0.9 for sediments (17), and are close to unity for most bottom sediments (5).

Equation 2 is solved to calculate D_s using the appropriate initial and boundary conditions for each of the three methods:

Method 1. The change in tracer concentration in the reservoir over time, assuming that the solution in the reservoir is thoroughly mixed and that the volume is fixed, is

$$\frac{\partial C_r}{\partial t} = \left(\frac{D_s \theta}{a_0} \frac{\partial C_s}{\partial x} \right) \bigg|_{x=0} \quad (5)$$

where a_0 is the height (L) of the solution reservoir. For this study a_0 was 1.24 cm for columns L1–L4 and 1.29 cm for columns L5–L7.

The appropriate initial and boundary conditions are given by

$$C_s(x, 0) = 0 \quad (6a)$$

$$C_s(\infty, t) = 0 \quad (6b)$$

$$C_s(0, t) = C_r(t) \quad (6c)$$

$$C_r(0) = C_0 \quad (6d)$$

Table I. Input Parameters To Calculate D_s for Each of the Methods

core	method 1a				method 1b t , days	method 2				method 3 t , days
	ρ , g cm ⁻³	θ , cm ³ cm ⁻³	a_0 , cm	t , days		L , cm	V_r , cm ³	V_p , cm ³	t , days	
L1	1.42	0.42	1.24	1.95	1.95					
L2	1.42	0.42	1.24	1.95	1.95					
L3	1.42	0.42	1.24	1.95						1.95
L4	1.42	0.42	1.24	1.96						1.95
L5	1.35	0.45	1.29	2.02		14.6	30	100.56	2.08	
L6	1.35	0.45	1.29	2.02		12.9	30	88.86	2.01	
L7	1.35	0.45	1.29	2.02		13.2	30	90.92	2.01	

The lower boundary condition, defined by eq 6b, assumes the column to be semiinfinite in length (or sufficiently long) such that the tracer concentration at the bottom of the column is always zero during the period of interest. Initially, the tracer concentration in the column is zero (eq 6a) with some C_0 in the reservoir (eq 6d). At the reservoir-sediment interface the tracer concentration is not constant but is equal to the reservoir concentration, which varies with time as shown in eq 6c.

Equations 2 and 5, subject to the initial and boundary conditions stated in eqs 6a–6d, can be solved analytically by the Laplace transform method (18). The solution for the reservoir concentration used in method 1a is

$$\frac{C_r(t)}{C_0} = \exp\left(\frac{\theta^2 R D_s t}{a_0^2}\right) \operatorname{erfc}\left[\frac{\theta(R D_s t)^{1/2}}{a_0}\right] \quad (7)$$

The analytical solution for the solute concentration in the sediment column for method 1b, using eqs 2, 5, and 6, is

$$\frac{C_s(x,t)}{C_0} = \exp\left(\frac{\theta R x}{a_0} + \frac{\theta^2 R D_s t}{a_0^2}\right) \operatorname{erfc}\left(\frac{R^{1/2} x}{(4 D_s t)^{1/2}} + \frac{\theta(R D_s t)^{1/2}}{a_0}\right) \quad (8)$$

where x is the distance (L) along the length of the column.

Equations 7 and 8 were fitted to measured changes in tracer concentrations in the reservoir (i.e., values of C_r/C_0 vs t) from method 1a and C_s/C_0 and x from method 1b (concentration profiles), respectively, with a nonlinear least-squares program (19) to calculate D_s values for tritium. The fitting procedure also calculated 95% confidence intervals for the D_s estimate based on all the data from each core. Core L1 was further analyzed by estimating D_s values for each successive sample, beginning with the third sampling time.

Method 2. For method 2, eq 2 was used with the following initial and boundary conditions:

$$C_s(x,0) = C_0 \quad (9a)$$

$$C_r(0) = 0 \quad (9b)$$

$$C_s(0,t) = C_r(t) \quad (9c)$$

$$\frac{\partial C_r}{\partial t} = \left(\frac{D_s \theta}{a_0} \frac{\partial C_s}{\partial x}\right) \Big|_{x=0} \quad (9d)$$

$$\frac{\partial C_s}{\partial x} \Big|_{x=\infty} = 0 \quad (9e)$$

The analytical solution, based on work by Crank (20)

and Stoessell and Hanor (9) and reported by McDuff and Ellis (10), is

$$\frac{C_r(t)}{C_0} = \left\{ 1 - \left[\exp\left(\frac{(D_s t) V_p^2}{l^2 V_r^2}\right) \operatorname{erfc}\left(\frac{(D_s t)^{1/2} V_p}{l V_r}\right) \right] \right\} \quad (10)$$

where V_p and V_r are the solution volumes (L^3) in the sediment column and reservoir, respectively, and l is the length (L) of the column. Note that $V_p/(V_r l) = \theta/a_0$; hence, eq 7 from method 1a is identical with eq 10 if the right-hand side of eq 7 is subtracted from unity.

Equation 10 was fitted to values of C_r/C_0 and t from the sediment-reservoir study with the nonlinear program (19) to calculate D_s values for tritium.

Method 3. For method 3, eq 2 is the governing equation (however, C_r is now C_0) with the following initial and boundary conditions for sediment to sediment diffusion:

$$C_s(x,0) = C_0; -\infty \leq x \leq 0 \quad (11a)$$

$$C_s(x,0) = C_i; 0 \leq x \leq +\infty \quad (11b)$$

$$C_s(-\infty,t) = C_0 \quad (11c)$$

$$C_s(\infty,t) = C_i \quad (11d)$$

where C_i is some initial solution concentration (ML^{-3}) in the nonspiked half-cell and C_0 is the initial concentration in the spiked half-cell. Values of C_i for method 3 were equal to zero.

By use of the analytical solutions presented by Crank (20), eq 2 and eqs 11a–11d can be transformed into

$$\frac{C_s - C_i}{C_0 - C_i} = 0.5 \operatorname{erfc}\left(\frac{x R^{1/2}}{(4 D_s t)^{1/2}}\right) \quad (12)$$

Values of C_s , C_0 , and x from the concentration profiles of each half-cell were fitted to eq 12 with the nonlinear program (19) to calculate D_s . Input parameters for the equations of each method are given in Table I.

Estimation of D_s . Diffusion coefficients using an empirical approach were also calculated as a comparison to laboratory estimates for the littoral sediment by using

$$D_s = D_0/(\theta F) \quad (13)$$

where D_0 is the diffusion coefficient in bulk water (ML^{-3}) and F is the formation resistivity factor (11). The formation resistivity factor, F , has been empirically related to θ such that (12)

$$F = \theta^{-m} \quad (14)$$

where m , an empirical constant, is a function of sediment type. Although values of m were not determined in this study, a value of 1.5 was used for this sandy sediment based on literature data (7).

Results

Tritium reservoir concentrations for method 1a decreased with time during the diffusion of tritium from a

Table II. Comparison of Tritium Diffusion Coefficients^a Estimated by Different Techniques

core	method 1a	method 1b	method 2	method 3
L1	1.36 (1.23-1.47)	1.23 (1.03-1.43)		
L2	1.55 (1.38-1.71)	1.14 (0.91-1.37)		
mean	1.46	1.19		
L3	1.63 (1.38-1.87)			1.02 (0.81-1.23)
L4	1.30 (1.03-1.57)			0.92 (0.71-1.11)
mean	1.47			0.97
L5	1.54 (1.26-1.82)		1.10 (0.83-1.36)	
L6	1.60 (1.29-1.91)		1.59 (1.42-1.76)	
L7	1.83 (1.49-2.19)		1.68 (1.36-2.00)	
mean	1.66		1.46	

^a In $\text{cm}^2 \text{ days}^{-1}$. ^b 95% confidence intervals in parentheses.

Table III. Comparison of Mean Values of D_s Estimated by Use of Successive Samples from Column L1^a

sample	time, days	D_s , $\text{cm}^2 \text{ day}^{-1}$	sample	time, days	D_s , $\text{cm}^2 \text{ day}^{-1}$
3	0.17	1.17 (1.09-1.26)	7	0.95	1.25 (1.10-1.40)
4	0.28	1.07 (0.90-1.26)	8	1.11	1.30 (1.16-1.44)
5	0.43	1.12 (0.99-1.26)	9	1.49	1.31 (1.20-1.43)
6	0.56	1.20 (1.04-1.36)	10	1.95	1.36 (1.23-1.48)

^a 95% confidence intervals in parentheses.

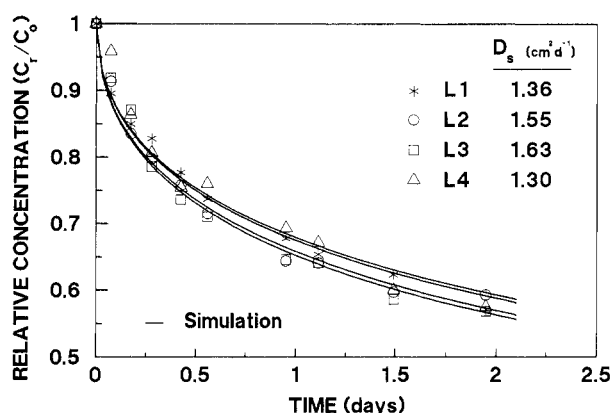


Figure 2. Diffusion of tritium in packed littoral sediments from Lake Okeechobee by the reservoir technique. Lines represent fitted simulations using eq 7.

spiked reservoir into a nonspiked sediment column (Figure 2). Estimated diffusion coefficients for the littoral sediments (cores L1-L7) from method 1a (eq 7) were similar and ranged from 1.30 to 1.83 $\text{cm}^2 \text{ day}^{-1}$ (Table II). These values were not significantly different from each other. As expected, all values of D_s were less than that measured for tritium diffusion in bulk water (D_0 is 2.11 $\text{cm}^2 \text{ day}^{-1}$ at 25 °C) (21). Tortuosity factors (τ) calculated from eq 5 ranged from 0.44 to 0.87 for the littoral sediment.

Sampling times for the diffusion experiment also affected estimates of D_s (Figure 3). For example, with core L1, D_s estimates beginning with the third sample increased when each successive sample was included into the fitting procedure. Estimates of D_s for the third through sixth sampling time (up to 0.5 day) were outside the 95% confidence intervals determined for D_s from all 10 samples; however, confidence intervals for all D_s estimates were overlapping with one another (Table III).

Sectioning of the sediment columns L1 and L2 (method 1b) immediately following the completion of method 1a yielded the tritium concentration profiles presented in Figure 4. The diffusion coefficients estimated from the

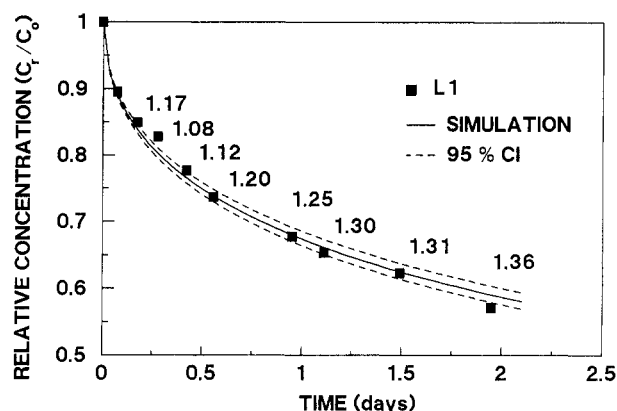


Figure 3. Tritium diffusion for core L1 by the reservoir method. Numbers represent D_s values ($\text{cm}^2 \text{ day}^{-1}$) calculated up to that sampling time. Solid lines represent fitted simulations using eq 7 and dashed line represents 95% confidence interval for D_s calculated with all the data.

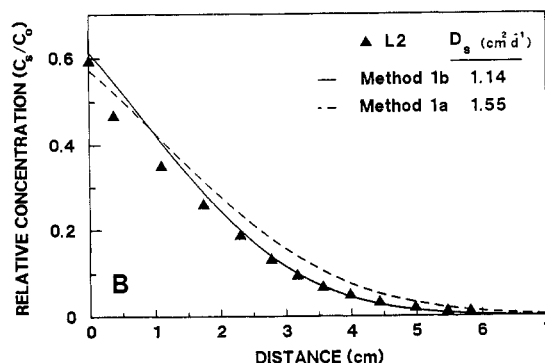
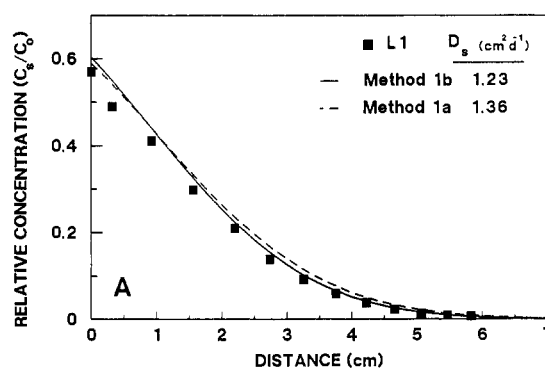


Figure 4. Tritium concentration profiles for the cores L1 (A) and L2 (B) immediately after the completion of the reservoir method. Simulation lines represent tritium concentration profiles based on D_s estimates calculated by the reservoir (eq 7, solid line) and concentration profile (eq 8, dashed line) methods.

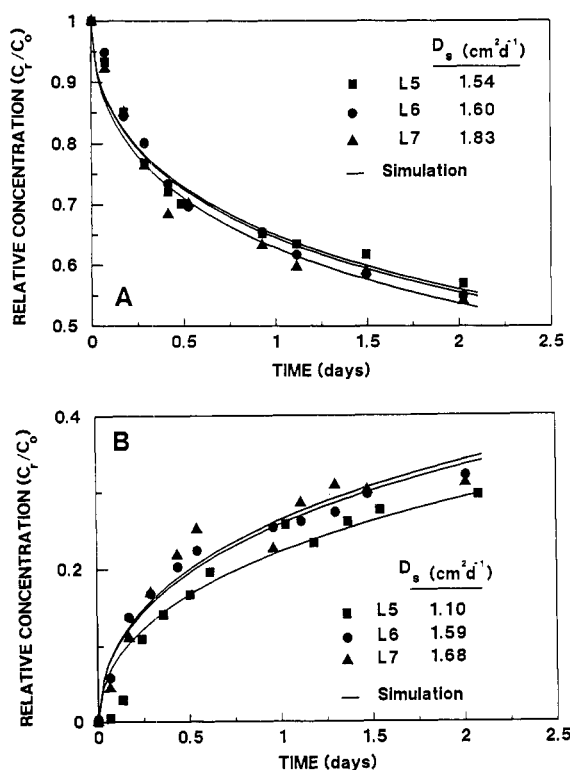


Figure 5. Tritium diffusion for undisturbed cores from littoral sediments by the reservoir (A) and sediment–reservoir methods (B). Solid lines represent fitted simulations using eq 7 and eq 10 for A and B, respectively.

concentration profile (eq 8) were 10–26% lower than those determined in method 1a (i.e., eq 7), especially for column L2 (Table II). Values of D_s determined by methods 1a and 1b were compared by simulating concentration profiles by use of eq 8. The simulated profiles were in agreement with the measured data for column L1 (Figure 4A); however, the simulated profile using D_s from eq 7 overestimated the concentration profile for column L2 (Figure 4B).

A comparison of tritium D_s using methods 1a and 2 is presented in Figure 5. Estimates of D_s measured by using eq 10 from method 2 were also lower (1–27%) than those determined by method 1a (eq 7) and ranged from 1.10 to 1.68 $\text{cm}^2 \text{day}^{-1}$ (Table II).

Values of D_s measured by method 3 (sediment–sediment diffusion) using eq 12 also underestimated D_s by 29–37% compared to those determined by method 1a (Table II). The concentration profiles for columns L3 and L4 from eq 12 were slightly shifted to the left of the experimental data (Figure 6A,B). Using D_s estimates from method 1a (eq 7) resulted in a slight counterclockwise rotation of the concentration profile to that calculated with the measured data (eq 12). Thus, the concentration profile in the cell with the spiked sediment was underestimated; however, profiles in the nonspiked cell were duplicated by the simulated profile (Figure 6A,B).

Theoretical values of D_s ranged from 1.38 to 1.42 $\text{cm}^2 \text{day}^{-1}$ when a θ of 0.42 $\text{cm}^3 \text{cm}^{-3}$ for cores L1–L4 and 0.45 $\text{cm}^3 \text{cm}^{-3}$ for cores L5–L7 was used. These values agreed well with those measured by method 1a, but were higher than those estimates determined by methods 1b and 3.

Discussion

Method 1a, based on solute diffusion from an overlying spiked reservoir into a saturated sediment column, is an effective technique when compared to the other methods for estimating diffusion coefficients of nonadsorbed tracers in lake sediments. The primary advantage of method 1a

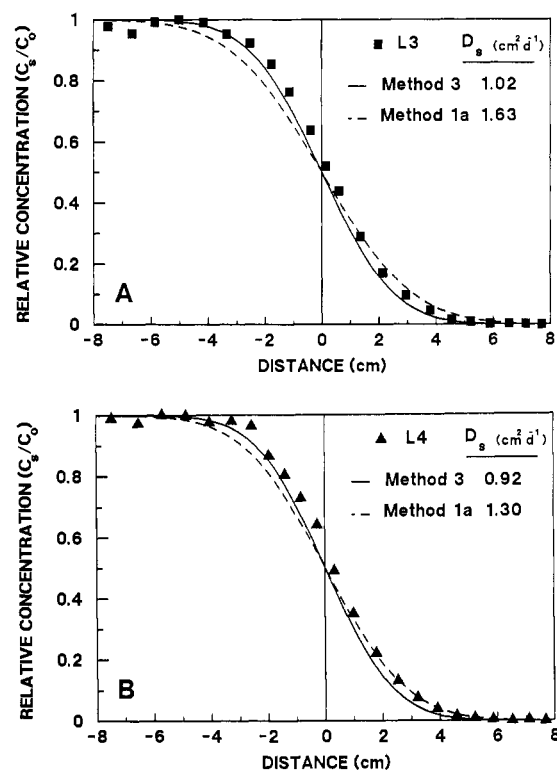


Figure 6. Tritium diffusion by the sediment–sediment technique for cores L3 (A) and L4 (B). Solid lines represent fitted simulations using eq 12 and dashed lines indicate simulation using D_s estimated from the reservoir method.

over methods 2 and 3 is that of time and simplicity. Sediments in method 1a do not need to be spiked; hence, experiments can be conducted quickly and efficiently, simply by initially spiking the reservoir solution and taking periodic samples. The other two methods, however, require more preparation time through first labeling the sediments prior to the experiment. Further verification of the D_s estimate measured in method 1a can also be facilitated by sectioning the column after the experiment is completed to yield a concentration profile, from which another estimate of D_s can be determined. The solute concentration profile data are also of interest in that they delineate the zone of sediment that has been influenced by diffusion.

A sensitivity analysis of eq 7 using data from this study revealed that a 10% error in the measurement of either the height of the water column (a_0) or the sediment water content (θ) resulted in a 20% difference in D_s . A 10% change in the retardation factor (R) resulted in a similar change in the D_s estimate. The errors in the D_s estimate associated with a 10% change in a_0 , θ , and R were in most cases within the 95% confidence interval predicted for the D_s estimate.

Both methods 1a and 2 have specific boundary conditions that require the reservoir solution to be well-mixed, whether by mechanical stirring or bubbling. This problem, however, was minimized in this study by reducing the height (a_0) of the reservoir to ~ 1 cm, hence eliminating any possible concentration gradient within the reservoir solution. One drawback to the small solution volumes in the reservoir is the effect on the sampling volume. In eqs 7, 8, and 10, it is assumed that the reservoir solution volume is constant during sampling; therefore, very small sample sizes are required. Radioisotopes facilitate the use of small sample volumes; however, analyses for some inorganic ions require larger sample volumes (ca. 3–5 mL). Ion-specific electrodes could be utilized to eliminate this

sampling problem. An analytical solution has been derived for conditions of large sample sizes with sample replacement (see Appendix); however, this condition was not specifically tested in this study.

In all three methods, the sediment columns are assumed to be semiinfinite in length. Methods 1a,b and 3 (non-spiked half-cell) require the tracer concentration constant (C_0 or C_i) at all times at the end of the column. For methods 2 and 3 the tracer concentration in the spiked half-cells is required to be constant (C_0) at all times at the end of the column. These boundary conditions should be validated by sectioning a column after the experiment; otherwise, sufficiently long cores should be used to avoid sectioning.

Another assumption common to all three methods is that the tracer diffuses through homogeneous sediments; however, this condition may not be valid, especially for undisturbed sediment cores due to sediment heterogeneity (i.e., sediment layering). D_s estimates, therefore, would represent an average value for the sediment depth to which the solute has diffused over the experimental period. Diffusion coefficients determined by any of the three methods, therefore, are valid only for the depth that the tracer has diffused (i.e., 6 cm as determined in method 1b).

Sorption-related parameters (i.e., K_d , R) used in solving the analytical solutions for each of the three methods assume that sorption is instantaneous and the isotherms are linear and reversible. These assumptions were not violated with tritium—a conservative, nonreactive tracer (i.e., $K_d = 0$; $R = 1$). For adsorbed tracers (i.e., $K_d > 0$; $R > 1$), however, caution must be exercised when D_s values are being calculated and interpreted. For example, phosphorus, which has been extensively studied in lake systems (8, 22), has isotherms that are nonlinear and is subject to considerable nonequilibrium, hence violating the required assumptions necessary to calculate D_s .

In this study, D_s estimates measured by method 1a were comparable after 0.5 day of diffusion (Figure 3), although the increasing estimates of D_s may be due to the optimization of D_s by the nonlinear program with time rather than some physical or chemical implications of the experiment itself. The time required, however, for an accurate estimate of D_s will be influenced by R , which incorporates the physical and chemical nature of the sediment and tracer, respectively. To determine when to terminate an experiment, we suggest that the limiting factor be defined by the depth of interest to which the solute front has diffused in the sediment, rather than the amount of solute mass that has been depleted from the reservoir. In this study the column length dictated the length of the experiment in order not to violate the bottom boundary condition (eq 3b). Therefore, if one is interested in D_s estimates for the top 6 cm of a sediment profile, an adsorbed solute will take much longer than that for a nonadsorbed tracer. Reactive solutes will then also require a larger mass for diffusion to reach a specified depth than that for nonreactive solutes due to sediment adsorption. Solute mass for reactive solutes can be increased by proportionally increasing a_0 with respect to R , until the height of the reservoir and solute mixing become restrictive. Otherwise another method, such as method 3, may be necessary.

Although the half-cell method (method 3) is most commonly used for diffusion estimates in unsaturated or saturated media, this method's major constraint is the time necessary for experimental setup and the measurements that are required when the cores are sectioned and the samples are centrifuged. A potential problem for method

3 is ensuring adequate contact between the sediment faces of two half-cells to facilitate the diffusion process. In this study, concentration profiles from both methods 1b and 3 had the lowest D_s estimates, suggesting that these methods may also be subject to more error through loss of solution or compression of the sediment during the extraction of the core from the column.

Practical Implications

Method 1a (reservoir technique) is a simple and effective method for quantifying diffusion coefficients for nonadsorbed solutes in freshwater or marine systems. This method is ideally suited for measuring diffusion coefficients on disturbed or intact (undisturbed) sediments in the laboratory; however, the experimental setup also lends itself to quantifying diffusion coefficients in situ in marine or freshwater sediments. In situ measurements would be advantageous in that they would provide (1) a means whereby one could investigate temporal and spatial variability of solute diffusion coefficients for sediments and (2) realistic estimates of D_s for use in whole-lake or diagenetic models (1, 23).

The experimental setup and boundary conditions for the reservoir technique are quite analogous to environmental scenarios where organic contaminants (24, 25), heavy metals, or nutrients (26) enter into the water system and are eventually transported across the sediment-water interface. The above applications are also valid for sediments that act as a source of pollutants should the chemicals desorb into the interstitial waters and subsequently diffuse into the overlying water (27). Method 2, however, would be the more applicable technique to measure these diffusion coefficients under laboratory or in situ conditions. Although adsorbed solutes were not tested here, the reservoir method could be applied to D_s measurements in sediment porewater for the above conditions provided that the necessary assumptions and boundary conditions are met and the experimental apparatus is compatible with the chemical of interest (i.e., stainless steel or Teflon containers for organic pollutants).

Active populations of benthic organisms can also have a significant effect on the effective diffusion coefficient as discussed earlier. Benthic organisms such as oligochaetes have been shown to impact pollutant transport via particle transport (D_b) (5); however, benthic organisms have also been implicated in solute transport via irrigation (D_i) of interstitial water during their respiration (2, 28). Measurement of solute transport by this process is difficult; however, the reservoir method, although not measuring a diffusion coefficient per se, is also relevant for quantifying D_i as influenced by the activity of the benthic organisms (4).

Method 1a or reservoir diffusion (reservoir to sediment), therefore is a technique comparable with other methods for measuring diffusion coefficients and it is hoped that the experimental setup and procedure will facilitate future research on diffusion coefficients of solutes in marine and freshwater sediments.

Appendix

The analytical solution for estimating D_s for large sample sizes with sample replacement in method 1a is as follows:

From mass balance considerations

$$V_r \frac{\partial C_r}{\partial t} = A \theta D_s \frac{\partial C_s}{\partial x} \Big|_{x=0} - V_s C_r \sum_{i=1}^{NT} \delta(t - t_i) \quad (\text{A-1})$$

where V_r and V_s are the volumes of the reservoir and sample, respectively; A is the surface area of the reservoir;

δ is the Dirac delta function; NT is the number of samples taken; and t_i is the sampling time for the i th sample. The initial condition for eq A-1 is

$$C_r(0) = C_0 \quad (\text{A-2})$$

By use of Laplace transforms (18), the analytical solution for the reservoir concentration for large sample volumes with sample replacement is

$$\frac{C_r(t)}{C_0} = \exp(\gamma^2 t) \operatorname{erfc}(\gamma t^{1/2}) - \frac{V_s}{V_r} \sum_{i=1}^{NT} C_r(t_i) \exp[\gamma^2(t - t_i)] \operatorname{erfc}[\gamma(t - t_i)^{1/2}]|_{t > t_i}$$

where

$$\gamma = \theta(RD_s)^{1/2}/a_0 \quad (\text{A-3})$$

The analytical solution (18) for the solute concentration in the sediment profile when large sample volumes are taken is

$$\frac{C_s(x, t)}{C_0} = \exp\left(\frac{\theta R x}{a_0} + \gamma^2 t\right) \operatorname{erfc}\left[\frac{R^{1/2} x}{2(D_s t)^{1/2}} + \gamma t^{1/2}\right] - \frac{V_s}{V_r} \sum_{i=1}^{NT} C_r(t_i) \exp\left[\frac{\theta R x}{a_0} + \gamma^2(t - t_i)\right] \operatorname{erfc}\left[\frac{R^{1/2} x}{2(D_s[t - t_i])^{1/2}} + \gamma(t - t_i)^{1/2}\right] \quad (\text{A-4})$$

Estimates of D_s can be calculated by fitting eqs A-3 and A-4 to the data.

Glossary

A	surface area of reservoir (L^2)
a_0	height of reservoir solution (L)
C_i	initial concentration of porewater (ML^{-3})
C_0	initial concentration of spiked solution (ML^{-3})
C_r	solute concentration in reservoir (ML^{-3})
C_s	solute concentration in porewater (ML^{-3})
D_b	biodiffusion coefficient (L^2T^{-1})
D_i	irrigation coefficient (L^2T^{-1})
D_0	diffusion coefficient in bulk liquid (L^2T^{-1})
D_s	molecular diffusion coefficient (L^2T^{-1})
D_{wc}	wave and current mixing coefficient (L^2T^{-1})
F	formation resistivity factor (dimensionless)
K_d	sorption coefficient (L^3M^{-1})
l	length of column (L)
m	formation resistivity factor power function
NT	number of samples
R	retardation factor (dimensionless)
t	time (T)
t_i	sampling time for i th sample
V_p	solution volume in sediment (L^3)
V_r	solution volume in reservoir (L^3)
V_s	sample volume (L^3)
x	distance (L)
ρ	soil bulk density (ML^{-3})
θ	volumetric water content (L^3L^{-3})
τ	tortuosity factor (L^2L^{-2})
δ	Dirac delta function
γ	$\gamma = \theta(RD_s)^{1/2}/a_0$

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