Geotechnical and Geological Engineering (2006) 24: 325–334
DOI 10.1007/s10706-004-7549-y

Investigations on diffusion characteristics of granite and chalk rock mass

KAI WITTHÜSER[1], DALINAIDU ARNEPALLI[2],
and DEVENDRA N. SINGH[2,★]
[1]*Department of Geology, University of Pretoria, Pretiria 0002, South Africa*
[2]*Department of Civil Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India*

(Received 25 August 2004; revised 29 November 2004; accepted 10 December 2004)

Abstract. Contaminant transport through fractured rock mass is predominated by diffusion. This is due to the continuous interaction of the mobile water present in the fracture network and relatively immobile pore water, which is adsorbed on the surface and in the rock matrix itself. Even though the advective flow through the fracture network is high, besides sorption of rock mass, the diffusive exchange into the rock mass leads to significant retardation of contaminant transport. Hence, for describing contaminant transport in fractured rock mass, more precisely, the effect of retardation attributed to the matrix diffusion must be taken in account. With this in view, a methodology, which can be employed for determination of the diffusion characteristics of the rock mass, has been developed and its details are presented in this paper. Validation of the methodology has been demonstrated with the help of Archie's law.

Key words. Archie's law, chalk, contaminant transport, diffusion, fractured rock mass, granite, waste disposal.

Notations

η	total porosity
ρ	bulk density
δ	constrictivity factor
α	rock capacity factor
τ	tortuosity factor
τ_s	tortuosity factor for saturated porous media
η_e	effective porosity
A	surface area of the rock sample
n	constant
c	concentration
$c(t)$	concentration at a time t
C_0	initial concentration of the solute
d	thickness of the sample

[★] Corresponding author: Devendra N. Singh, Professor, Department of Civil Engineering, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India. e-mail: dns@civil.iitb.ac.in

D'	relative diffusivity
D_a	apparent diffusivity
D_e	effective diffusivity
D_m	free-water molecular diffusivity
D_p	pore diffusivity
G	specific gravity
J_d	diffusive mass flux
K_d	distribution coefficient
L	straight flow path
L_e	tortuos flow path
t	time
V	volume of the receiving cell
x	distance
ξ	empirical parameter
m	cementation factor

1. Introduction

One of the basic causes of contamination of the rock mass is deep disposal of highly toxic radioactive waste (Chapman and McKinley, 1987). In case of interconnected fractures, the contaminant transport is through the fracture network itself even though their volume as compared to the total volume of the rock mass is negligible (Neretnieks, 1980). Hence, advection dominates contaminant transport through such type of the rock mass. However, the contaminant transport in highly porous rock matrix and less interconnected fractured network is predominantly by diffusion (Lever and Bradbury, 1985). In other words, contaminant transport in a well-connected-fracture network is driven by pressure gradients, termed as advection, whereas transport in the porous rock matrix is driven by concentration gradients, termed as diffusion (Bigersson and Neretnieks, 1990). In order to describe contaminant transport in the fractured rock mass, these transport processes have to be coupled hence the effect of matrix diffusion must be incorporated and quantified (Lever and Bradbury, 1985). This calls for establishing the diffusion characteristics of the rock mass.

With this in view, an attempt was made in this paper to develop a simple methodology, which can be employed for a sufficiently precise estimation of diffusion characteristics of chalk and granite rocks using the Archie's law.

2. Diffusion through porous media: governing equations

In general, molecular diffusion describes the net mass transfer by random molecular motion of the contaminant due to concentration gradient(s) existing on either side of the diffusing substance(s) (Crank, 1975). Mathematically, the one-dimensional mass diffusive flux, J_d, of a solute in water due to a concentration gradient can be described using Fick's 1st law:

$$J_d = -D_m \frac{\partial c}{\partial x} \tag{1}$$

where D_m is the molecular diffusion coefficient, c is the concentration and and x is the distance.

The diffusive transport of contaminant(s) through the porous rock matrix exhibits several complex interactions between the matrix, the water molecules and the contaminant. The mobility of a solute through the pore water of a rock matrix considerably reduces, under the influence of physical interaction with the matrix and the geometrical constraints, such as constricted (constrictivity factor, δ), elongated and tortuous (tortuosity factor, τ) diffusive transport paths, is described by the pore diffusion coefficient, D_p (Neretnieks, 1980):

$$D_p = D_m \frac{\delta}{\tau} \tag{2}$$

The tortuosity factor, τ, is usually defined as (Carman, 1956):

$$\tau = (L_e/L)^2 \tag{3}$$

where L_e is the actual length of the tortuous flow path and L is the length of the straight flow path. Saripalli et al. (2002) have defined the tortuosity factor for saturated porous media, τ_s, as the ratio of the measurable specific surface area of the medium to its specific surface area of an idealized capillary bundle. Their definition, based on measured (using BET method) interfacial areas, incorporates already the constrictivity factor, which must be omitted in Equation 2 if τ_s is used in a theoretical capillary bundle.

As some pores in the rock matrix are 'dead end pores' (Lever et al., 1985), or are too small in diameter to contribute to the diffusive flux, the effective or transport porosity, η_e, is usually smaller than the total accessible porosity, η. The effective porosity, the empirical constrictivity and the tortuosity factors can be summarized to the relative diffusivity, D', which describes the diffusive properties of a porous rock mass itself. The relation between different diffusion coefficients is given by Neretnieks (1980):

$$D_e = D_p \eta_e = D_m \eta_e \frac{\delta}{\tau} = D_m D' \tag{4}$$

For one-dimensional stationary diffusive mass flux, J_d, of a solute in a porous saturated medium follows:

$$J_d = -D_e \frac{\partial c}{\partial x} = -D_m D' \frac{\partial c}{\partial x} \tag{5}$$

Since sorption only prolongs the transient or instationary phase of the diffusion in a porous medium, Fick's 1st law is valid for solutes that exhibit sorption, only. The instationary diffusive transport of a sorbing or non-sorbing solute in the porous medium, can be described by Fick's 2nd law:

$$(\eta + \rho K_d)\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} \tag{6}$$

where ρ is the bulk density of the porous medium and K_d is the distribution coefficient of a linear sorption isotherm (Henry, 1922). The term in parentheses is usually termed as the capacity factor, α, which describes the solute holding capacity of the porous medium. For non-sorbing substances, the capacity factor equals the total accessible porosity, η, as K_d value becomes zero. Defining the apparent diffusivity, D_a, as:

$$D_a = \frac{D_e}{\alpha} = D_p \tag{7}$$

leads to the following expression:

$$\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2} \tag{8}$$

The relative diffusivity, D', of the rock mass can also be estimated with help of Archie's law (Archie, 1942), by knowing the total porosity of the rock mass and the rock mass specific cementation factor, m:

$$D' = \frac{D_e}{D_m} = \xi \cdot \eta^m \tag{9}$$

For the sake of simplicity, the empirical factor, ξ, is typically taken as unity (Ullmann and Aller, 1982). Nevertheless, its value depends on the characteristics of the porous medium and its value may not be equal to unity (Iversen and Jørgensen, 1993; Barker, 1994).

3. Determination of the diffusion coefficient

Different methods, which are employed for determining diffusion characteristics of the rock mass can be classified as: In situ measurements by employing the tracer techniques (Käss, 1998) or laboratory experiments on the representative samples. The in situ determination of the diffusion characteristics in natural fractured rock mass requires sophisticated instrumentation: injection and detection systems (Becker and Shapiro, 2000), apart from being time and cost intensive. In such a situation, laboratory experiments are found to be a better alternative. However, development of appropriate mathematical model(s) for these experiments is quite essential. For these reasons, diffusion coefficient determined from the in situ tests, often, do not match with those obtained by laboratory experiments. Nevertheless, only field investigations can verify if laboratory results are representative of the investigated part of the aquifer.

Laboratory experiments are usually performed as in-/out- or through-diffusion experiments. In in-diffusion experiments (Skagius and Neretnieks, 1988), the diffusive flux is observed from a reservoir of high solute concentration into a rock sample (with a known initial solute concentration, which is usually maintained as zero) or the distance that a contaminant has diffused into the rock sample from a reservoir of constant concentration is observed. In out-diffusion experiments (Tits et al., 2003), the reverse process is observed, i.e. the diffusive flux from a rock sample with initially known solute concentration is observed. However, either of these tests would yield the apparent diffusion coefficient by describing the concentration development in the reservoir with an appropriate solution of Fick's 2nd law (Crank, 1975). In through-diffusion experiments (Feenstra et al., 1984), the diffusive flux is observed between a reservoir cell with high concentration across a porous rock sample and a receiving cell with an initial concentration of zero. The analytical solution of Fick's 2nd law for through-diffusion experiments, outlined below, yields the effective diffusion coefficient and the capacity factor of the rock sample, and hence also the apparent diffusion coefficient (using Equation 7). It must be noted that simultaneous determination of diffusion and retardation properties of the rock mass is the advantage of through-diffusion experiments. In- or out-diffusion experiments will not produce these coefficients, making sorption experiments necessary to distinguish between the contribution of sorption and diffusion to the apparent diffusion coefficient.

4. Experimental investigations

Chalk samples from Israel and Denmark, and granite samples from India were tested for their diffusion characteristics by conducting experiments with strontium, Sr^{2+}, and sodium, Na^{+}, in their chloride form as contaminants. Throughout experimentation, the ambient temperature and relative humidity were maintained as 26 ± 1.5°C and 50%, respectively. These samples were characterized for their specific gravity (with the help of a Ultra Pycnometer) and total porosity (with the help of a Mercury intrusion porosimeter).

Diffusion cell, as depicted in Figure 1, has been fabricated and used in the present study. The cell is made of Perspex and consists of two reservoirs, a source reservoir, depicted as 1, and a receiver reservoir, depicted as 2. These reservoirs are separated by a sample holder, which is made of Perspex and can hold a circular rock sample. Before starting experiments, rock samples are saturated by soaking them in degassed Millipore water for at least six weeks. Reservoir 1 is filled with 0.01 M solution ($= C_0$) of the contaminant (in present study, $SrCl_2$ and NaCl), and the concentration of contaminant (Sr^{2+} and Na^{+}) is monitored in Reservoir 2, which is filled with KCl isotonic solution, initially. KCl solution helps in reducing/eliminating density driven fluxes (Bradbury and Green, 1985). To ensure no hydraulic gradient acts across the sample, standpipes are fitted to these reservoirs and same height of the solutions is maintained in them. For detection of Sr^{2+} and Na^{+}, an ICP unit has been employed and sampling of the solution from Reservoir 2 has been done by withdrawing 10 cc of the solution. After each withdrawal, 10 cc of isotonic solution is replaced in the Reservior 2 and proper correction has been applied for the changes occurring in the concentration (Gurumoorthy and Singh, 2004).

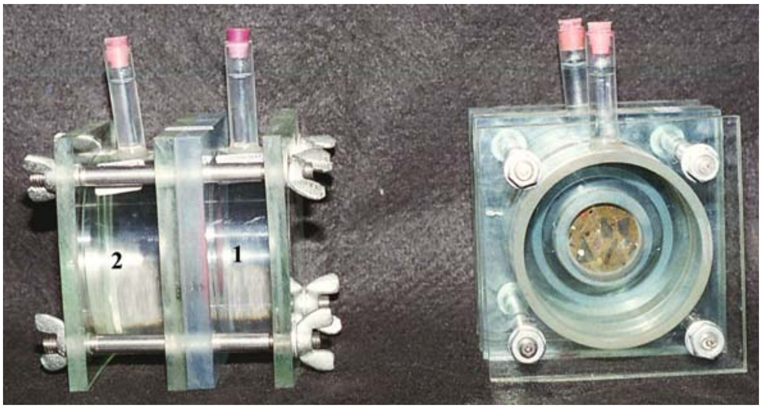

Figure 1. Diffusion cells fabricated and used in the present study.

5. Results and discussions

Table 1 presents details of the rock samples used in this study. Experimental observations i.e., the concentration of diffused ion in Reservoir 2, $C(t)$, for all nine samples was recorded as a function of time, t. For the sake of brevity, a typical breakthrough curve (BTC) for diffusion of Sr^{2+} through 10 mm thick Israeli chalk sample is presented in Figure 2. From the figure, it can be noted that after an initial transient phase, during which the contaminant partly accumulates in the rock matrix due to sorption and dead end pores (Lever et al., 1985), $C(t)$ increases linearly with time.

An analytical solution for Equation 8, has been proposed by Carslaw and Jaeger (1959):

$$C(t) = \frac{AdC_0}{V}\left(\frac{D_e t}{d^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{\eta^2}\exp\left[\frac{-D_e\eta^2\pi^2 t}{\alpha d^2}\right]\right) \tag{10}$$

where C_0 denotes the concentration of the solution in the Reservoir 1, V is the volume of the Reservoir 2, d and A are the thickness and surface area of the rock

Table 1. Physical properties of the various samples used in the study

Sample	Rock type	Source	d (mm)	G	η
1	Chalk	Israel	10.7	2.65	0.3525
2			10.5	2.70	0.3721
3			10.0	2.67	0.3782
4			8.7	2.70	0.3717
5			8.1	2.88	0.3880
6		Denmark	14.4	2.80	0.4419
7			12.2	2.90	0.4737
8	Granite	India	7.0	3.00	0.0574
9			6.9	2.94	0.0349

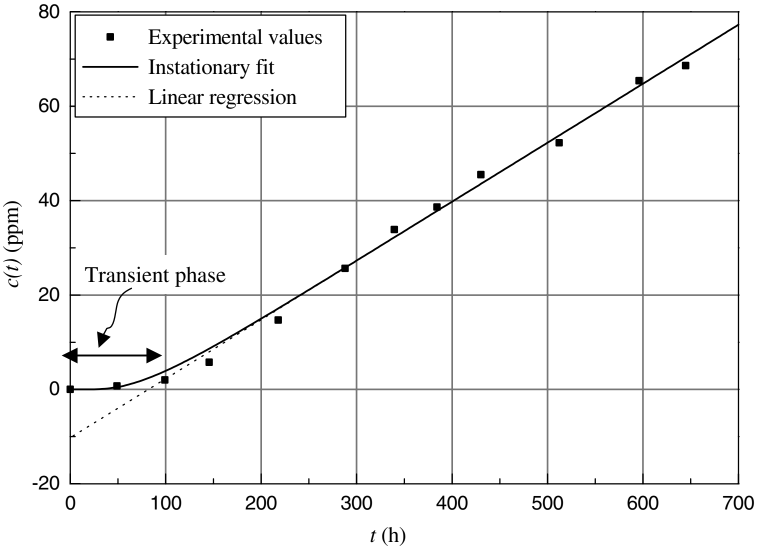

Figure 2. A typical breakthrough curve for Sr^{2+} diffusion through chalk sample.

sample, respectively. The diffusion parameters such as, effective diffusivity, D_e, and the capacity factor, α, can be obtained from Figure 2, as discussed in the following.

Equation 10 takes into account the transient phase of the breakthrough curve, i.e. the time to develop a linear concentration gradient in the rock sample, in determining of the effective diffusion coefficient and the capacity factor. However for the stationary phase of the experiment ($t \rightarrow \infty$), the exponential term becomes zero and the following simplified relationship can be obtained (Bradbury and Green, 1985):

$$C(t) = \frac{AC_0D_\mathrm{e}}{Vd}t - \alpha\frac{AdC_0}{6V} \tag{11}$$

hence, D_e and α can be determined by using the slope of the linear portion of the break through curve (Figure 2), and its intercept with the ordinate.

Using Equations 10 and 11 (in case of insufficient data in the instationary part of the BTC), and test specific A and V values, D_e and α have been determined and their values are listed in Table 2. The relative diffusion coefficient, D', of these rock samples has also been obtained with the help of Equation 9. The free molecular diffusion coefficient, D_m, for Sr^{2+} and Na^+ has been taken as 7.94×10^{-10} m^2/s and 1.33×10^{-9} m^2/s, respectively (Skagius and Neretnieks, 1986). Following this, Equation 9 has been fitted to the results reported by Witthüser et al. (2003) for Israeli chalk samples, and the value of rock cementation factor, m is found to be 2.57, as depicted in Figure 3. For validation of the obtained results, and the developed methodology, experimentally obtained D' values for Israeli chalk samples (Samples 1–5) have also been superimposed in the figure. An excellent matching between the

Table 2. Experimental results

									m	
Sample	Rock mass	Source	Tracer	A(cm^2)	V(cc)	$D_e \times 10^{-13}$ (m^2/s)	α	D'	Computed value	Reported value
1	Chalk	Israel	Sr^{2+}	22.06	299.0	591.3	2.04	0.0745	2.49	2.57[a]
2				22.06	287.5	740.1	2.17	0.0932	2.41	
3				22.58	302.0	644.7	1.78	0.0812	2.58	
4				22.06	293.0	614.4	1.27	0.0774	2.59	
5				21.24	300.0	729.8	1.24	0.0919	2.53	
6		Denmark	Na^+	14.78	275.0	1766	3.96	0.1328	2.47	
7			Sr^{2+}	15.00	285.0	1177	0.89	0.1482	2.55	
8	Granite	India	Sr^{2+}	15.21	286.0	99.8	0.06	0.0126	1.53	1.54[b]
9				14.93	287.5	60.0	0.12	0.0076	1.46	

[a]Witthüser et al. (2003); [b]Skagius and Neretnieks (1986)

results can be observed. Incidentally, value of m obtained for these chalk samples, and listed in Table 2, is also found to be quite close to 2.57. For Danish chalk samples also the value of m is found to be 2.47 and 2.55, which are quite close to 2.57. This indicates that the developed methodology is quite efficient in determining diffusion characteristics of the chalk samples investigated.

Attempts were also made to develope Archie's law for granite rock mass. To achieve this, results of the diffusion experiments on granite with Na^+ and Sr^{2+} as contaminants, which are available in litetarure, as depicted in Figure 4, have been used (Skagius and Neretnieks, 1986). As depicted in the figure, the value of m is found to be 1.54. Incidentally, experimentally obtained results for granite rock samples (Samples 8 and 9) yield values of m as 1.53 and 1.46, respectively.

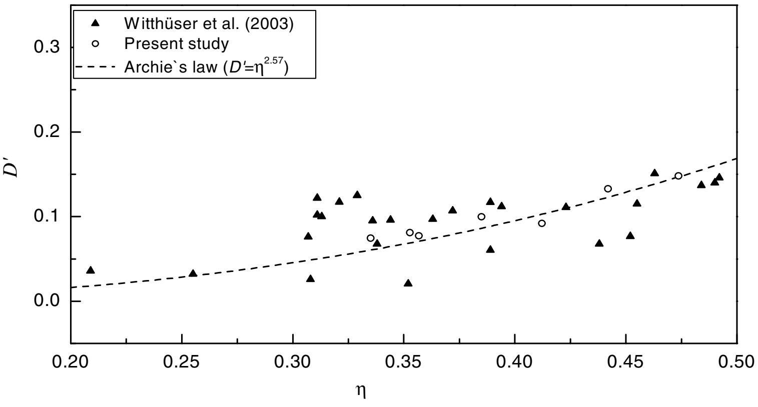

Figure 3. Variation of the relative diffusion coefficient with porosity for the samples of the chalk rock mass.

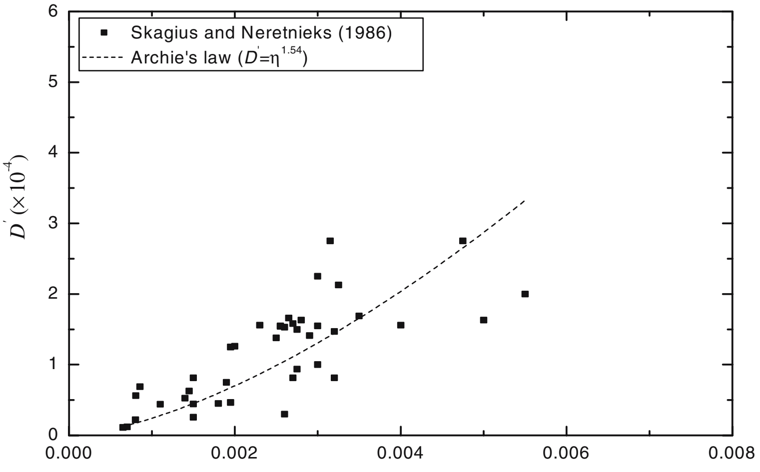

Figure 4. Variation of the relative diffusion coefficient with porosity for the samples of granite rock mass.

6. Concluding remarks

Based on the results and discussion presented in this paper, it can be concluded that the methodology to determine diffusion characteristics of the rock mass is quite efficient and can be used for determining Archie's law parameters for different types of the rock mass. The factor ξ and cementation factor, m, for the granite rock mass are found to be unity and 1.54, respectively. Using these parameters, diffusion coefficient of a contaminant in granite rocks can be determined, easily.

Acknowledgement

This work was supported by a fellowship within the Postdoc-Programme of the German Academic Exchange Service (DAAD).

References

Archie, G. E. (1942) The electrical resistivity log as an aid in determining some reservoir characteristics, *Trans. Am. Inst. Min. Met. Petr. Eng.*, **146**, 54–62.

Barker, R. D. (1994) Some hydro geophysical properties of the chalk of humberside and Lincolnshire, *Quarterly J. Eng. Geol.*, **27**, S5–S13.

Becker, M. W. and Shapiro, A. M. (2000) Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing, *Water Resour. Res.*, **36**(7), 1677–1686.

Birgersson, L. and Neternieks, I. (1990) Diffusion in the matrix of granitic rock: Field test in the Stripa Mine, *Water Resour. Res.*, **26**(11), 2833–2842.

Bradbury, M. H. and Green, A. (1985) Measurement of important parameters determining aqueous phase diffusion rates through crystalline rock matrices, *J. Hydro.*, **82**, 39–55.

Carman, P. C. (1956) *Flow of gases through porous media*, Academic Press Inc., New York.

Carslaw, H. S. and Jaeger, J. C. (1959) *Conduction of heat in solids*, Clarendon Press, Oxford.

Chapman, N. and McKinley, I. G. (1987) *Geological disposal of nuclear waste,* Wiely.

Crank, J. (1975) *The mathematics of diffusion*, Clarendon Press, Oxford.

Feenstra, S., Cherry, J. A., Sudicky, E. A. and Haq, Z. (1984) Matrix diffusion effects on contaminant migration from an injection well in fractured sandstone, *Ground Water*, **22**(3), 307–316.

Gurumoothy, C. and Singh, D. N. (2004) Experimental methodology to assess contaminant diffusion in rock mass, *Environ. Monit. Assess.*, **91**, 277–291.

Henry, D. C. (1922) A kinetic theory of adsorption:, *Philos. Mag. Ser.* **6**(44), 689–705.

Iversen, N. and Jørgensen, B. B. (1993) Diffusion coefficients of sulfate and methane in marine sediments: influence of porosity, *Geochim. Cosmochim. Acta* **57**, 571–578.

Käss, W. (1998), *Tracing Technique in Geohydrology*, A. A. Balkema, Lisse.

Lever, D. A. and Bradbury, M. H. (1985) Rock-matrix diffusion and its implications for radionuclide migration, *Mineralogical mag.*, **49**, 245–254.

Lever, D. A., Bradbury, M. H. and Hemingway, S. J. (1985) The effect of dead-end porosity on rock-matrix diffusion, *J. Hydrol.,* **80**, 45–76.

Neretnieks, I. (1980) Diffusion in the Rock Matrix: An important factor in radionuclide retardation, *J. Geophys. Res.*, **85**(B8), 4379–4397.

Saripalli, K. P., Serne, R. J., Meyer, P. D. and McGrail, B. P. (2002) Prediction of diffusion coefficients in porous media using tortuosity factors based on interfacial areas, *Ground Water,* **40**, 346–352.

Skagius, K. and Neretnieks, I. (1988) Measurement of cesium and strontium diffusion in biotite gneiss, *Water Resour. Res.*, **24**(1), 75–84.

Skagius, K., and Neretnieks, I. (1986) Porosities and diffusivities of some nonsorbing species in crystalline rocks' *Water Resour. Res.*, **22**, 389–398.

Tits, J., Jacob, A., Wieland, E. and Spieler, P. (2003) Diffusion of tritiated water and $^{22}Na^+$ through non-degraded hardened cement pastes, *J. Contam. Hydrol.*, **61**, 45–62.

Ullmann, W. J. and Aller, R. C. (1982) Diffusion coefficients in near shore marine sediments, *Limnology Oceanogr.*, **27**(3), 552–556.

Witthüser, K., Reichert, B. and Hötzl, H. (2003) Contaminant transport in fractured chalk: laboratory and field experiments', *Ground Water*, **41**(6), 806–815.