

Diffusion of Iodide in Low Permeability Clayey Soils

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Transport through the low permeable lenses is governed by diffusion and has been found very critical in remediation of hazardous waste sites especially the ones with common groundwater contaminants like trichloroethylene (TCE) or tetrachloroethylene (PCE). Although diffusion through clayey layers is such an important process, the diffusion coefficient in saturated clayey soils is generally estimated with procedures developed for sandy soils without considering the unique component of clay soils: clay minerals. Clay minerals have extremely small particle size and negatively charged surfaces which significantly increase the tortuosity and causes charge-dependent transport. In order to fulfill the gap in experimental data about diffusion in clay soils and serve as the baseline to examine the diffusion of common organic contaminants such as TCE, the diffusion coefficient of iodide was measured in saturated silt and silt-Na-montmorillonite clay mixtures by a steady state procedure known as the time-lag method. The average effective diffusion coefficient of iodide was determined to be in a range of 1.02 to 2.00×10^{-6} cm²/sec. Besides, comparison of the experimental results with the estimations demonstrated that methods estimating the diffusion coefficient as a function of porosity overestimated the experimental data severely (>350% relative error).

Keywords: Clayey soils, Diffusion, Iodide, Na-montmorillonite, Remediation.

Introduction

Chlorinated dense non-aqueous phase liquids (DNAPLs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) are two of the most common organic contaminants detected at Superfund sites (SERDP and ESTCP, 2006). Those immiscible and dense contaminants move downward in the subsurface rather than being transported laterally as a dissolved plume and pool on the low permeable layers, i.e. aquitards. Further transport into the low permeable lenses is dominated by diffusion because of the negligible rate of advection through these layers (Goodall and Quigley, 1977; Johnson et al., 1989). Through diffusion, a significant mass of DNAPLs can accumulate in low permeability lenses over time which turns these layers into contamination storage areas.

DNAPL pooled on top of the aquitards is expected to deplete and the concentration in the groundwater is expected to decrease by the groundwater flow or remedial action yet that is not what is observed in the field. This

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phenomenon is a consequence of “back diffusion” (Chapman and Parker, 2005) which is the rerelease of the accumulated contaminants from the aquitard into the surrounding groundwater upon removal of the DNAPL pool. Studies such as that by Parker et al., 2008 show that even a clay layer thinner than 0.2 m can result in groundwater concentrations above permissible levels for decades after the original source is isolated or removed. Moreover, simulations suggest that the contaminant concentrations in groundwater might not be reduced below the maximum contaminant level (MCL) even after decades of aquifer remediation (Ball et al., 1997; Chapman and Parker, 2005; Parker et al., 2008). Thus, these low permeable lenses and layers may serve as long-term secondary contamination sources (Sale et al., 2008; Stroo et al., 2012). As a result of these studies within the last two decades revealing the impact of low permeable lenses on the remediation of the DNAPL contaminated sites, diffusion of chlorinated solvents into aquitards has gained a lot of attention.

Even though diffusion is such a critical process in terms of remediation of hazardous waste sites contaminated with DNAPLs, the effective diffusion coefficient is not usually measured; rather it is estimated based on the correlations suggested in the literature (Ball et al., 1997; Parker et al., 2004). Empirical methods (Table 1) have been proposed to estimate the ratio of the effective diffusion coefficient to the aqueous diffusion coefficient, or the relative diffusivity, as a function of porosity. The correlations summarized in Table 1 were developed for the diffusion of a gas or inorganic solute in unsaturated sandy soils. Adaption of such relations to the transport in saturated soils can be possible by assuming that the total pore volume is filled with water. The relative diffusivity described by Millington and Quirk models then became:

$$\frac{D_e}{D_{aq}} = \varepsilon^{4/3} \tag{Equation 1}$$

Table 1. Methods for the Determination of Relative Diffusivity, D_e/D_{aq}

Method	Reference
0.66a	Penman (1940)
$a^{3/2}$	Marshall (1959)
$\frac{a^2}{\varepsilon^{2/3}}$	Millington and Quirk (1960)
$\frac{a^{10/3}}{\varepsilon^2}$	Millington and Quirk (1961)
$\frac{a^{3.1}}{\varepsilon^2}$	Sallam et al. (1984)

ε : total porosity; a: volumetric air content

As it can be seen, the estimation methods suggest an exponential increase in effective diffusion coefficient with increasing porosity. However, it is known that the low permeable clay soils with higher porosity have a lower diffusion coefficient (Grathwohl, 1998; Itakura et al., 2003). The problems related with the use of these correlations to estimate relative diffusivities in clay soils

have been recognized by Olesen et al. (1999) who reported that the performance of the estimation with Millington-Quirk correlation was degraded when applied for soils with clay content higher than 21%. Also, the experimental results that exist in the literature were compared with estimations produced by the models given in Table 1 and it was reported that the relative diffusivity of organic solutes in water-saturated low permeable soils were overestimated by the correlations with a minimum relative error of 130% (Ayril and Demond, 2014). This issue might be originated from the fact that low permeable clay layers consist of significant amount of clay minerals which differ distinctly from inert sandy soils owing to their smaller size, and negatively charged surface. These properties of clay minerals hinder the total porosity from being a good indicator of volume available for diffusion in clay soils and limit the accuracy of porosity-based correlations. Tinnacher et al. (2016) reported that pore scale models with single porosity fail to explain the microstructure of clayey media. First of all, diffusion-accessible porosity is affected by the charge of the solute because of the negative charge of the clay surfaces. Repulsive force between the negatively-charged solute and the surface of the clay might exclude anions from the pores. This phenomenon is called “anion exclusion”, and recent research found that it is affected not only by the average pore size, but also by a combination of parameters such as pore size distribution, pore throat size, connectivity of the pores and (stress-related) narrowing as well as widening of the pores (Tournassat et al., 2016, Jacobs et al., 2017). As a result, diffusion-accessible porosity for anions may be 3-100 times smaller than the total porosity (Appelo and Wersin, 2007; García-Gutiérrez et al., 2004; Montavon et al., 2009; Shackelford and Moore, 2013; Van Loon and Mibus, 2015) than the one for neutral species depending on the dry bulk density of the bentonite soil.

As the diffusion-accessible porosity is equal to the total porosity for the uncharged species, one can expect that the porosity-based correlations could work for neutral solutes. However, water in the micropores and some fraction of the macropores of clay minerals might not be available for diffusion (Shackelford and Moore, 2013). Yang and Aplin (2010) stated that the pore radii of clay minerals are much smaller than sand soils even though the overall porosity is higher. Thus, the relative diffusivity in clay soils may be smaller than in sandy soils due to the smaller pore size and resultant greater tortuosity, despite the larger porosities. Moreover, smaller pore radius and the resulting high surface area are reported to cause lower permeability due to increased friction (Adams et al., 2016).

Furthermore, some types of clay minerals may have variable porosities depending on their degree of compaction. As total porosity is problematic in estimating the relative diffusivity in clay soils, a number of studies have addressed the relationship between the diffusivity of inorganic solutes and the bulk density of clay materials. The bulk density was used since it reflects the degree of compaction which in turn affects the diffusion-accessible porosity in clay minerals. Ayril and Demond (2014) developed a log-linear correlation using the literature data for HTO diffusion in montmorillonite compacted to

different bulk densities from García-Gutiérrez et al., 2004; Miyahara et al. 1991; and Sato et al., 1992. The combined data yields:

$$\log\left(\frac{D_e}{D_{aq}}\right) = -0.8549\rho_b - 0.0868 \quad (\text{Equation 2})$$

Bourg et al. (2006) described another alternative method to estimate the relative diffusivity as the weighted average of the relative diffusivities in macropores and interlayer space. Assuming that the constrictivity of macropores is equal to 1 and the geometric factor for the macropores and interlayer space is the same, they proposed that the relative diffusivity in montmorillonite can be given by:

$$\frac{D_e}{D_{aq}} = \frac{(1-f_{\text{interlayer}})+\delta_{\text{interlayer}}f_{\text{interlayer}}}{G} \quad (\text{Equation 3})$$

where G is a geometric factor that has a value of 4.0 for both macropores and interlayer space, δ , the constrictivity of the interlayer space, has a value of 0.3, and $f_{\text{interlayer}}$ is the fraction of porosity in the interlayers. The fraction of interlayer pores as a function of bulk density is given in Bourg et al. (2006). Ayral and Demond (2014) fitted piecewise linear models to Bourg et al.'s (2006) data and obtained the following:

$$f_{\text{interlayer}} = 0.87\rho_b - 0.348, \text{ for } 1 < \rho_b < 1.3 \text{ g/cm}^3 \quad (\text{Equation 4})$$

$$f_{\text{interlayer}} = 0.78 \text{ for } 1.3 < \rho_b < 1.5 \text{ g/cm}^3 \quad (\text{Equation 5})$$

$$f_{\text{interlayer}} = 0.9\rho_b - 0.58, \text{ for } 1.5 < \rho_b < 1.7 \text{ g/cm}^3 \quad (\text{Equation 6})$$

The latter two models based on the bulk density were reported to improve the performance of the estimation for organic solute diffusion in clayey soils by reducing the relative error to 16-63% (Ayral, 2015).

As pointed out earlier, the diffusion coefficient is a crucial parameter for models utilized in remediation projects because it is the process that determines groundwater concentrations and the time required for remediation. The diffusion coefficients in saturated clay soils were estimated due to an insufficient amount of measured values. These estimations might not be appropriate to use if the soil medium include clay minerals. Therefore, measurement of the effective diffusion coefficient of iodide in a saturated clayey soil becomes the first goal of this study. This diffusion coefficient would also serve as a baseline while investigation of diffusion of chlorinated organic solutes in saturated clay soils. Also, the measured diffusion coefficients were compared with the estimates to evaluate the validity of the correlations for saturated soils including clay minerals.

Materials and Methods

Preparation of Soil Samples

Silica silt and clay minerals were used to prepare two different types of soil matrices for diffusion measurements. The first soil matrix was silica silt with a median diameter of 10 μm , and a SiO_2 content of 99.7% (U.S. Silica, Frederick, MD). The second soil matrix was a combination of silica silt and pure Na-montmorillonite clay (SWy-2, cation exchange capacity (CEC) is 76.4 meq/100 g) (Clay Minerals Society, Chantilly, VA) to represent the presence of reactive clay minerals in aquitard materials. The determination of the relative quantities of each was based on the quantities cited as occurring in aquitards and the swelling potential. Ball et al. (1997) reported a clay fraction of 17-35% in the aquitard at Dover AFB, and Murray and Quirk (1982) stated that soil mixtures with a clay content of less than 30% can accommodate volume changes within the pores of the matrix. To satisfy both criteria, 25% was chosen as the clay fraction for the silt-clay mixtures.

The soils were packed dry in a ring (I.D: 5 cm, height: 1 cm) in seven layers, compacting each layer with a 2.5 cm diameter wooden rod for producing homogeneous packed columns. The dry bulk density was calculated from the mass of the soil packed in the ring (about 35 gram) and the volume of the ring (22.5 cm^3). The porosity of the samples was then determined from the bulk dry density assuming that the density of the solid was equal to 2.65 g/cm^3 .

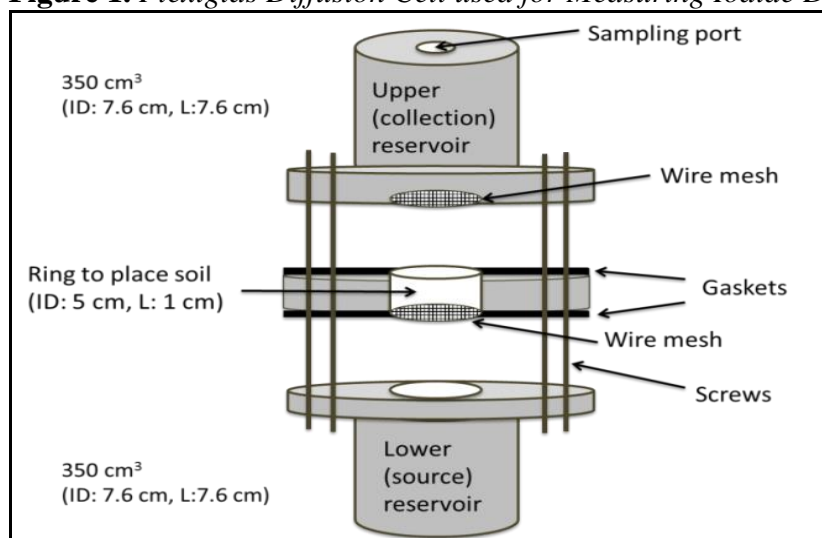
The ring then was placed on top of a reservoir which was filled with a 0.005 M CaSO_4 solution for saturation. A 0.005 M CaSO_4 solution was used rather than distilled water since distilled water is reported as problematic in hydraulic conductivity experiments (ASTM D5856-95, 2007). The silt in the ring stayed in contact with the water for one day to allow the spontaneous imbibition of water from the bottom of the sample to the top, and the change in the weight of the ring was recorded. Following that, the water level in the reservoir was raised to induce seepage through the porous medium to eliminate air that might be remaining. At the end of the second day, the weight of the ring was checked again, and since the change in mass was insignificant it was considered that saturation had been achieved.

Silt-clay mixtures were packed by the same method described for the silt, and then two different approaches were used for saturation. The first one entailed placing a stainless steel block with a weight about 0.5 kg on top of the soil to help ensure even swelling. After ten days of imbibition of the water from the bottom, the change in the mass became negligible (change $< 1\%$). Then, the portion of the soil that swelled beyond the top of the ring was scraped off, the air was dried and then weighed to calculate the porosity after expansion. Then, on the tenth day, the level of the reservoir was raised and maintained for another week to displace any remaining air. The second saturation method for silt-clay mixtures restricted the expansion of the soil even more. The soil mixture in the ring was placed on the reservoir filled with water while confined at the top, so the sample could not swell beyond the confines of the ring and the total volume

could not change. As a result, the porosities of the samples treated in this manner were lower than the porosities of the silt-clay samples which were allowed to expand.

Diffusion Experiment

Figure 1. Plexiglas Diffusion Cell used for Measuring Iodide Diffusion



The design of the diffusion cell was based on Boving and Grathwohl (2001). It was constructed of Plexiglas and contained three main sections (Figure 1). The lower reservoir served as the source; the middle section consisted of a ring with a 5.0 cm internal diameter and a height of 1 cm to hold the porous medium, and a top reservoir collected the material that had diffused through the porous medium. Each of the two reservoirs had a volume of about 350 cm³. This volume was considered to be large enough to prevent significant concentration changes in the source and collection reservoirs during the experiments (Boving and Grathwohl, 2001), thus maintaining a constant concentration gradient across the sample. Stainless steel mesh (TWP, Berkeley, CA) with a pore size of 2 μm was placed on both the top and the bottom of the ring to keep the solid particles of the porous medium out of the reservoirs. The ring containing the compacted and saturated soil was placed on top of the source reservoir filled with a 0.1 M potassium iodide solution. Iodide solution was obtained by dissolving potassium iodide (Sigma Aldrich, >99.5%) in Milli-Q water which was created by passing deionized, distilled water through a series of four Milli-Q filters and had a resistivity of 18.3 MΩ·cm. The upper reservoir was filled with a 0.1 M potassium nitrate (Sigma Aldrich, >99%) solution, in order to provide a similar osmotic potential in both reservoirs and eliminate the transport of solutes due to osmotic potential gradients. The upper reservoir was placed on top of the ring and the three components of diffusion cell were assembled by tightening the screws. Every day, the diffusion cell was rotated to minimize the development of concentration gradients within the reservoirs.

Iodide concentrations over time were measured in the upper collection

reservoir using an iodide selective probe (Ionplus, Thermo Scientific, Beverly, MA) connected to an Orion Five Star Meter (Thermo Scientific, Beverly, MA). The cumulative mass of iodide in the collection reservoir was calculated from the concentration measured by the iodide probe and the volume of the collection reservoir (350 cm³).

Diffusion in such a system can be modeled as diffusion in plane sheet which is initially free of solute ($C_1 = 0$, $x > 0$, $t = 0$). The concentration at the boundary at the source is at a constant concentration for times greater than $t = 0$ ($C = C_0$, $x = 0$, $t > 0$) and the concentration at the collection boundary of the plane sheet is zero ($C = C_2 = 0$, $x = d$, $t > 0$). As time approaches infinity, i.e. at a steady state, the effective diffusion coefficient in this plane sheet under the constant concentration gradient can be determined to be (Crank, 1975; Grathwohl, 1998):

$$D_e = \frac{d}{C_0} \frac{dM}{dt} \quad (\text{Equation 7})$$

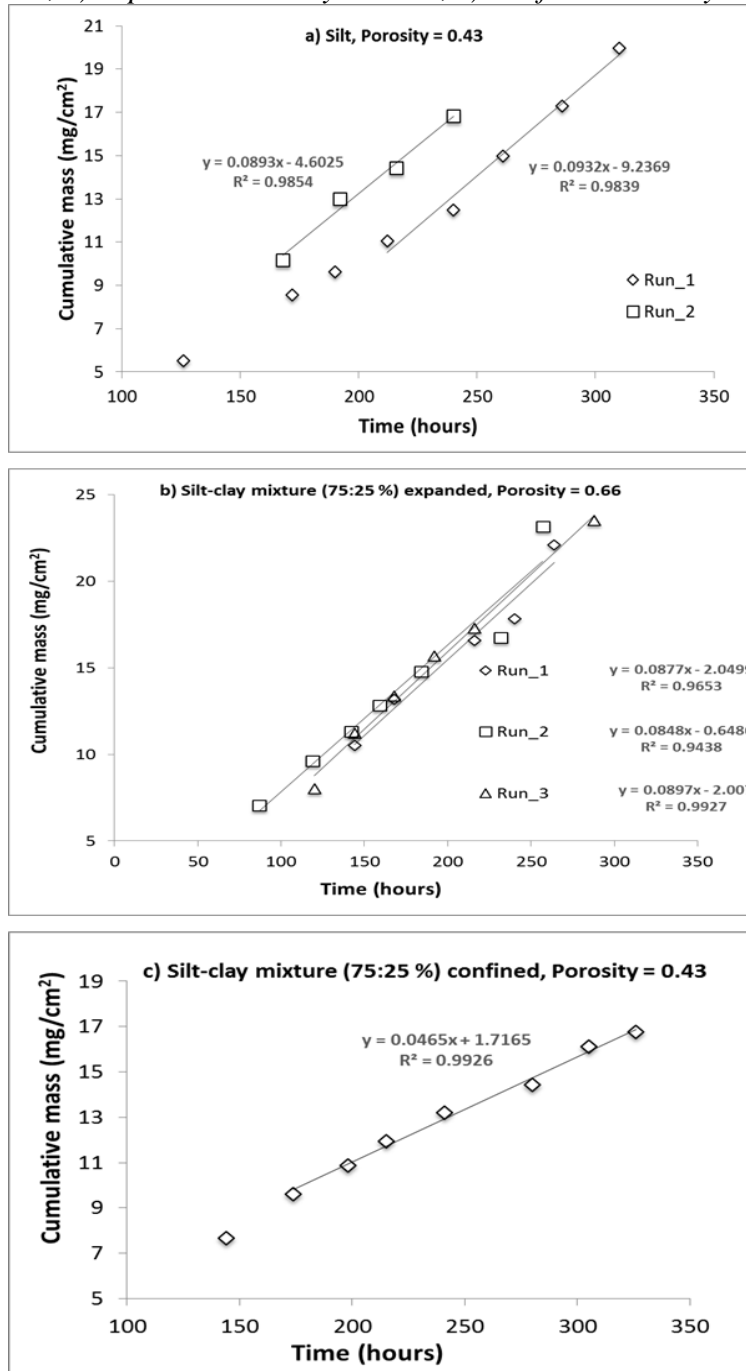
Therefore, with the observation of cumulative mass change over time in the collection reservoir, known thickness of the soil specimen ($d=1\text{cm}$) and the concentration at the source reservoir ($C_0= 12690 \text{ mg/L}$), the effective diffusion coefficient of iodide was calculated for each set of the experiments.

Results and Discussion

The main goal of the iodide experiments was contribution of the effective diffusion coefficient of a tracer on which the diffusion coefficient of TCE would be based. Comparison of these experimental diffusion coefficients with the estimations was also aimed because there was a need to examine the applicability of estimation methods for clayey soil. Figure 2 a, b, and c show plots of the cumulative mass of iodide that diffused through the silt, expanded silt-clay mixture and confined silt-clay mixture, respectively as a function of time. The average effective diffusion coefficient of iodide was determined to be $2.00 \times 10^{-6} \pm 6.04 \times 10^{-8} \text{ cm}^2/\text{sec}$ for silt, and $1.91 \times 10^{-6} \pm 5.39 \times 10^{-8} \text{ cm}^2/\text{sec}$ for the silt-clay mixture that was allowed to expand during saturation (Table 2). These measurements are comparable to reported effective diffusion coefficients for iodide such as that of $1.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ for bentonite with a porosity of 0.49 (Cho *et al.*, 1993) and $5.3 \times 10^{-6} \text{ cm}^2/\text{sec}$ for a natural smectitic clay compacted to a porosity of 0.46 (Shackelford and Daniel, 1991). The relative standard deviation was smaller than 5%, indicating reproducible results. These results are not significantly different (p -value > 0.15 at 95% confidence level) which suggests that the presence of 25% clay in and of itself did not reduce the diffusion rate of iodide significantly. However, in the case of the silt-clay mixture that was not allowed to expand freely, the effective diffusion coefficient of iodide decreased significantly (p -value < 0.15) to $1.02 \times 10^{-6} \text{ cm}^2/\text{sec}$. Since the silt and confined silt-clay mixture had the same porosity of 0.43, it is apparent that clay content affected the diffusion rate substantially. Thus, estimating the diffusion coefficient based on the porosity

would fail to predict the difference. Furthermore, the silt-clay mixtures have the same clay content, yet the diffusion coefficient was reduced in the confined sample, due to the lower porosity of the confined sample ($\epsilon = 0.43$) compared to the porosity of the expanded mixture ($\epsilon = 0.66$). Therefore, neither clay percentage nor porosity alone is sufficient to describe the diffusive characteristics of a clayey soil.

Figure 2. Cumulative Mass per Unit Area vs Time for Iodide Diffusion through a) Silt, b) Expanded Silt-Clay Mixture, c) Confined Silt-Clay Mixture



Effective diffusion coefficients can be estimated by using the relations summarized in Table 3. The methods developed for unsaturated sandy soils (Penman; 1940; Marshall, 1959; Millington and Quirk, 1960; Millington and Quirk, 1961; Sallam et al., 1984) have been reported to overestimate the relative diffusivity in clayey soils and the same behavior was observed in the case of the measurements here, with a relative error of > 350%. Equations 2-6, which were suggested as providing more accurate estimates for clayey soils, performed better in estimating the relative diffusivity of iodide. The log-linear fit to the literature results for tritiated water estimated the relative diffusivity of iodide both in expanded and confined in silt-clay mixtures with the smallest relative error (35% overestimation and 24% underestimation, respectively). Although anion exclusion was considered as the reason of lower diffusion of anions in clay formations (Wigger and Van Loon, 2017), it could not be evaluated whether the fact that the measured diffusion coefficients are lower than the estimated values is due to anion exclusion because the general tendency of the methods is to overestimate the diffusion coefficients.

Table 2. Average Effective Diffusion Coefficients for Iodide in Different Soils

Porous medium	Average porosity	Average D_e (cm ² /sec)	Standard deviation (cm ² /sec)	Relative standard deviation (%)	Average relative diffusivity (D_e/D_{aq})
Silt	0.43	2.00×10^{-6}	6.04×10^{-8}	3.0	0.11
Silt and clay mixture, expanded	0.66	1.91×10^{-6}	5.39×10^{-8}	2.8	0.10
Silt and clay mixture, confined	0.43	1.02×10^{-6}	NA	NA	0.05

D_e calculated using Equation 7, assuming that $C_o = 12690$ mg/L (0.1 M KI) and $d = 1$ cm. Relative standard deviation = standard deviation/average, $D_{aq} = 18.6 \times 10^{-6}$ cm²/sec (Robinson and Stokes, 1959), NA: not applicable since single experimental value

Table 3. Comparison of Relative Diffusivities for Iodide Measured in this Study and Estimated by Methods Summarized in Table 1, and Equations 2-6

Models	Average percent relative error (%)		
	Silt	Silt-clay expanded	Silt-clay confined
Penman (1940)	164 (0.28)	324 (0.44)	418 (0.28)
Marshall (1959)	162 (0.28)	422 (0.54)	414 (0.28)
Millington and Quirk (1960; 1961)	202 (0.32)	460 (0.57)	492 (0.32)
Sallam et al. (1984)	268 (0.40)	517 (0.63)	621 (0.40)
Log-linear fit to data (Equation 2)	61* (0.04)	35 (0.14)	24* (0.04)
Bourg et al. (2006) (Equation 3-6)	6 (0.11)	69 (0.17)	107 (0.11)

*Underestimation.

Numbers in parentheses are relative diffusivity estimated by the method.

Conclusions

Diffusion is the key process to understand the transport in the low permeable aquitards. Thus, the effective diffusion coefficient in low permeable soils is the most essential parameter required in models of subsurface remediation. Nevertheless, this significant parameter is commonly estimated due to the scarcity in measured values. The correlations estimate the effective diffusion coefficient as an exponential function of the porosity of soil and were reported to over predict the experimental data. In this study, the effective diffusion coefficient of iodide in saturated clayey soils was determined experimentally. It appeared that the correlations grossly overestimate the diffusion coefficient, especially in soils with clay content higher than 25%. Two other estimation methods were also explored: a log-linear relationship developed by fitting experimental data for the diffusion of tritiated water in clay soils and a theoretical relation by Bourg et al. (2006) developed for clay soils considering clay variables such as the fraction of interlayer space. Both of these estimation methods performed better in estimating relative diffusivities of iodide. So, it is clear that these methods should be preferred whenever there is an urge to estimate the effective diffusion coefficient in a clay soil. Furthermore, the reported effective diffusion coefficients of a tracer could act as a reference for diffusion of organic solutes.

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