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Light reflection visualization to determine solute diffusion into clays

Minjune Yang [a], Michael D. Annable [b], James W. Jawitz [a,*]

[a] Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA
[b] Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL 32611, USA

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ABSTRACT

Light reflection visualization (LRV) experiments were performed to investigate solute diffusion in low-permeability porous media using a well-controlled two-dimensional flow chamber with a domain composed of two layers (one sand and one clay). Two different dye tracers (Brilliant Blue FCF and Ponceau 4R) and clay domains (kaolinite and montmorillonite) were used. The images obtained through the LRV technique were processed to monitor two-dimensional concentration distributions in the low-permeability zone by applying calibration curves that related light intensity to equilibrium concentrations for each dye tracer in the clay. One dimensional experimentally-measured LRV concentration profiles in the clay were found to be in very good agreement with those predicted from a one-dimensional analytical solution, with coefficient of efficiency values that exceeded 0.97. The retardation factors (R) for both dyes were relatively large, leading to slow diffusive penetration into the clays. At a relative concentration $C/C_0 = 0.1$, Brilliant Blue FCF in kaolinite ($R = 11$) diffused approximately 10 mm after 21 days of source loading, and Ponceau 4R in montmorillonite ($R = 7$) diffused approximately 12 mm after 23 days of source loading. The LRV experimentally-measured two-dimensional concentration profiles in the clay were also well described by a simple analytical solution. The results from this study demonstrate that the LRV approach is an attractive non-invasive tool to investigate the concentration distribution of dye tracers in clays in laboratory experiments.

1. Introduction

The fate and transport of contaminants in groundwater systems are governed by complex physical and chemical processes such as advection, dispersion, diffusion, and sorption. Among these, diffusion has been recognized as one of the most fundamental processes controlling contaminant transport in clay and porous rock matrices (Foster, 1975; Gillham et al., 1984; Mackay and Cherry, 1989). For example, recent work has shown that storage and subsequent release from low-permeability zones may be important contributors to the long-term persistence of groundwater contaminant plumes (Chapman and Parker, 2005; Liu and Ball, 2002; Parker et al., 2008). Storage can be defined as the mass movement of contaminants from an area of greater concentration in high-permeability zones toward areas of lower concentration in low-permeability zones in a heterogeneous groundwater system. Release can then be defined as mass transfer from low-permeability zones to high-permeability zones due to the reversal of the concentration gradient following displacement or removal of the contaminants from the high-permeability zone (Chapman and Parker, 2005). This diffusion process will continue as long as a concentration difference exists, even in the absence of fluid flow.

Given the difficulty in gathering detailed data in the field, controlled laboratory experiments have provided a useful tool to investigate contaminant transport processes. Several

* Corresponding author. Tel.: +1 352 294 3141; fax: +1 352 392 3902.
E-mail address: Jawitz@ufl.edu (J.W. Jawitz).

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recent modeling and laboratory studies have demonstrated the importance of storage and release processes that cause plume persistence. Brown et al. (2012) developed a one-dimensional diffusion model to describe the storage and release of contaminants from aquitards given dynamic concentration boundary conditions. Chapman et al. (2012) investigated diffusion into and out of low-permeability zones using a laboratory tank tracer test and numerical modeling. They used fluorescein to visualize storage and release processes, although the tracer concentrations in the clay were not determined in their study. Wilking et al. (2013) also conducted a tank experiment to monitor contaminant mass depletion using X-ray photon attenuation and evaluate plume longevity related to mass storage in low-permeability zone.

Laboratory flow chamber experiments, coupled with image analysis techniques for quantification of spatial and temporal contaminant dynamics in porous media, have been used successfully as a non-destructive optical dye measurement technique (Corapcioglu and Fedirchuk, 1999; Gaganis et al., 2005; Huang et al., 2002; Jia et al., 1999; Jones and Smith, 2005; Theodoropoulou et al., 2003). Measurements can be made by gamma ray attenuation (Tidwell and Glass, 1994; Tuck et al., 1998), X-ray attenuation (Glover et al., 2007; Hilpert et al., 2000), and light transmission or reflection (Catania et al., 2008; Jaeger et al., 2009; Konz et al., 2009; Wang et al., 2008). However, methods using X and gamma ray require costly equipment for the measurements and may be prohibitively expensive. The challenge for light transmission techniques is collecting experimental data using non-transparent media materials such as clay and silt.

Although a number of researchers have reported success in transparent porous media involving light transmission/reflection visualization methods, applications have not been reported on non-transparent media such as clay. Furthermore, despite the importance of diffusion in transport processes between low- and high-permeability zones, there is little information linking image analysis to diffusion between clay and sand zones. Hence, this study presents well-controlled flow chamber experiments coupled with the light reflection visualization (LRV) method to investigate diffusion of two dyes (Brilliant Blue FCF and Ponceau 4R) in two clays (kaolinite and montmorillonite) between high- and low-permeability zones. Experimental results were compared to one-dimensional analytical solutions for dye concentration diffusion profiles in clay.

2. Methods

2.1. Selection of dye tracers and clays

Brilliant Blue FCF and Ponceau 4R (Sigma-Aldrich) are respectively blue and red dyes with maximum absorption wavelengths at 630 nm and 506 nm. Biological degradation of both of these synthetic dyes is expected to be insignificant due to the absence of enzymes necessary to decompose them under aerobic conditions in the natural system (Zollinger, 2003). Photochemical degradation of both dyes in aqueous solutions is also assumed to be negligible due to their relative stability under light exposure (Pagga and Brown, 1986; Porter, 1973; Zollinger, 2003). Further, the experiments were conducted in dark-room conditions and were only exposed to light during imaging. In addition, Ponceau 4R is known to be chemically stable, and easily soluble (Jaeger et al., 2009).

In an effort to select appropriate dye tracers to use in controlled laboratory experiments, simple batch adsorption tests were conducted. The results of these tests showed that the amount of Brilliant Blue FCF adsorbed on montmorillonite was 3.3 times larger than that on kaolinite while the amount of Ponceau 4R adsorbed on montmorillonite was 1.4 times larger than that on kaolinite (data not shown). A visual, qualitative diffusion experiment is illustrated in Fig. 1. Test tubes were partially filled with saturated clays and 5 mL aliquots of solutions of both dyes were carefully placed on top of the clays. The photographs in Fig. 1 were taken after 14 days. The diffusion front for Brilliant Blue FCF advanced visibly farther in kaolinite than in montmorillonite because of the much larger sorption in montmorillonite, where the bulk of the dye accumulated near the interface between the clay and the dye solution. Brilliant Blue FCF, which is a weak acid organic dye with polar and non-polar components, was adsorbed into the interlayer space of montmorillonite, a smectite expanding-lattice 2:1-type clay (Yermiyahu et al., 2002, 2003). Specific surface area, which has a strong influence on dye adsorption in clay, is much higher for montmorillonite (700–800 m^2/g, including internal and external surfaces) than kaolinite (5–30 m^2/g), which is a 1:1 silicate clay and has a relatively low cation exchange capacity (CEC = 3–15 $cmol_c/kg$) (Brady and Weil, 2008; Liu and Zhang, 2007). The sorption of Ponceau 4R was similar in both clays, and thus this dye showed no optical changes between kaolinite and montmorillonite (Fig. 1). Although a diffusion front of this red dye was not clearly visible on either clay in Fig. 1, it was found that the red color in both clays could be detected in the LRV process. Therefore, Ponceau 4R was selected as the dye tracer for montmorillonite while Brilliant Blue FCF was used in kaolinite.

2.2. Dye tracer experiments

Two dye tracer experiments were performed: the first with Brilliant Blue FCF and kaolinite, and the second with Ponceau 4R and montmorillonite. The flow chamber used in this experiment was similar to that described by Wang et al. (2008) with a 12 cm high by 28 cm long frame formed using 1.2 cm square aluminum tubing which was enclosed by two sheets of glass (28 cm × 10 cm). The aluminum tubing was slotted (slot width 0.03 cm) to serve as injection and extraction wells. The chamber was packed with two different materials: a 4-cm bottom layer of 20/30 mesh Accusand (Unimin Corp.), covered by a 6-cm top layer of kaolinite or montmorillonite. Dry sand and clay were introduced into the top of the flow chamber using a funnel and were deposited into standing water to minimize air trapping.

A Brilliant Blue solution containing 230 mg/L and a Ponceau 4R solution containing 200 mg/L were displaced through the flow chamber for 23 days. Fig. 2 shows a schematic of the flow chamber system. Dyes were delivered to the injection well under steady-state flow conditions maintained by a constant head reservoir (5 L Mariotte bottle). Effluent was collected in a fraction collector at the average flow rate of about 0.02 mL/min for Brilliant Blue FCF and 0.01 mL/min for Ponceau 4R. The absorbance for Brilliant Blue and Ponceau 4R was measured using a microplate reader (BioTeK Synergy H1 Hybrid Reader).