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## Variability of organic carbon content and the retention and release of trichloroethene in the rock matrix of a mudstone aquifer

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### ABSTRACT

Contaminants diffusing from fractures into the immobile porosity of the rock matrix are subject to prolonged residence times. Organic contaminants can adsorb onto organic carbonaceous materials in the matrix extending contaminant retention. An investigation of spatial variability of the fraction of organic carbon ( $f_{oc}$ ) is conducted on samples of rock core from seven closely spaced boreholes in a mudstone aquifer contaminated with trichloroethene (TCE). A total of 378 samples were analyzed at depths between 14 and 36 m below land surface. Mudstone units associated with deep water deposition have the largest  $f_{oc}$ , with a maximum value of 0.0396, and units associated with shallow water deposition have the smallest  $f_{oc}$ . Even though  $f_{oc}$  correlates with depositional conditions,  $f_{oc}$  still varies over more than an order of magnitude in continuous mudstone layers between boreholes, and there is large variability in  $f_{oc}$  over short distances perpendicular to bedding. Simulations of diffusion and linear equilibrium adsorption of TCE using spatially variable  $f_{oc}$  in the rock matrix show order of magnitude variability in the adsorbed TCE over short distances in the matrix and residence times extending to hundreds of years following remediation in adjacent fractures. Simulations using average values of  $f_{oc}$  do not capture the range of TCE mass that can be retained in a rock matrix characterized by spatially variable  $f_{oc}$ . Bounds on TCE mass within the rock matrix can be obtained by simulations with spatially uniform values of  $f_{oc}$  equal to the maximum and minimum values of  $f_{oc}$  for a given mudstone unit.

### 1. Introduction

The use of chlorinated solvents at many federal, industrial and commercial facilities over the past several decades has resulted in widespread groundwater contamination (Pankow et al., 1996, McCarty, 2010). In fractured rock aquifers, characterizing the spatial extent and longevity of contamination and designing effective remediation strategies has been particularly challenging (NAS, 2015). Fractures control the spatial extent of contamination; however, aqueous phase constituents can diffuse from fractures into the immobile fluid within the primary porosity of the rock (also referred to as the rock matrix). When concentration gradients are conducive, constituents diffuse back into permeable fractures and migrate down gradient, resulting in degraded water quality to down gradient receptors over decades to centuries (Mutch et al., 1993, Chapman and Parker, 2005, Sale et al., 2008).

In addition to diffusive exchange between fractures and the rock matrix, the retention of chlorinated solvents in fractured rock is also controlled by adsorption partitioning between the aqueous phase and solid surfaces associated with fracture walls or within the rock matrix. A linear equilibrium model is frequently applied in characterizing the adsorption of organic compounds (Allen-King et al., 1996),

$$C_s = K_d C_{aq} \quad (1)$$

where  $C_s$  is the concentration of the constituent in the adsorbed phase,

$C_{aq}$  is the concentration of the constituent in the aqueous phase, and  $K_d$  is the partitioning coefficient defined as (Cwierty and Scherer, 2010)

$$K_d = K_{oc} f_{oc} \quad (2)$$

where  $K_{oc}$  is the constituent's equilibrium partitioning coefficient defining its susceptibility to adsorb to organic carbon. The equilibrium adsorption model leads to the definition of a retardation factor,  $R$  (Domenico and Schwartz, 1990),

$$R = 1 + \frac{\rho_b}{n} K_d = 1 + \frac{\rho_b}{n} K_{oc} f_{oc} \quad (3)$$

where  $\rho_b$  is the bulk density of the aquifer material and  $n$  is the porosity. The retardation factor scales the diffusive flux relative to constituents that do not adsorb to aquifer materials (Freeze and Cherry, 1979). More complex models of the adsorption have also been proposed to account for the nonlinearity of adsorption over a larger range of aqueous concentrations (Allen-King et al., 2002, Huang et al., 2003). In this investigation, however, we consider only the application of a linear equilibrium adsorption model.

Identifying  $f_{oc}$  is a critical component in site characterization to evaluate the significance of the adsorption of organic contaminants (Kueper et al., 2003). Sedimentary rocks can exhibit variations in  $f_{oc}$  depending on the rock type (Gehman, 1962) and depositional environment (Lacombe and Burton, 2010). Calm, deep water

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environments support aquatic life in the water column while providing anoxic conditions upon deposition that suppress the decomposition of organic materials. In contrast, shallow waters often exhibit turbidity and wave action that limit the growth of aquatic vegetation and promote dissolved oxygen and decomposition. Thus,  $f_{oc}$  can vary between classifications of sedimentary rocks depending on the composition of the sediments and the depositional environment associated with those sediments. ITRC (2015) provides a compilation of values of  $f_{oc}$ , explicitly noting characteristics of unconsolidated sediments and rock types. However, even within a given type of sedimentary rock, for example, sandstone versus mudstone, changing depositional conditions can give rise to variations in the content of organic materials in the lithified rock (Lacombe and Burton, 2010).

The significance of quantifying  $f_{oc}$  in sedimentary rocks to evaluate the retention and release of organic contaminants from the rock matrix is widely recognized (Kueper et al., 2003, ITRC, 2015). In comparing the mass of aqueous and adsorbed TCE in a mudstone, Shapiro et al. (2017) concluded that adsorption is responsible for the majority of TCE retained in the rock matrix, indicating that assigning representative values of  $f_{oc}$  is critical in quantifying the retention of organic contaminants. In many instances, representative values of  $f_{oc}$  are determined from a small number of rock samples, usually by taking an average and combining those results with representative values of other parameters to estimate a retardation factor associated with the rock matrix (Kueper et al., 2003, Sterling et al., 2005). Several previous investigations have addressed the effect of spatially variable formation properties on the adsorption of chemical constituents; however, these investigations have focused primarily on the variability of these properties along groundwater flow paths (Valocchi, 1989, Cvetkovic and Shapiro, 1990, Rajaram, 1997). The retention and release of organic contaminants by diffusion in the matrix of sedimentary rocks due to spatial variability of  $f_{oc}$  within the rock matrix has not been fully investigated.

The purpose of this investigation is to demonstrate the range of spatial variability in  $f_{oc}$  in a fractured mudstone aquifer and the control that depositional conditions have on the magnitude and variability of  $f_{oc}$ . The significance of that variability in the retention and release of TCE from the rock matrix is demonstrated through simulations of TCE diffusion into and out of the rock matrix, and comparisons are made to simulations using average values of  $f_{oc}$ . This investigation uses  $f_{oc}$  analyses from rock samples collected from seven closely spaced boreholes in the upper 36 m of the mudstone aquifer underlying the former Naval Air Warfare Center (NAWC), West Trenton, NJ (Fig. 1). Variability in  $f_{oc}$  with depth in individual boreholes is investigated, along with the areal continuity of  $f_{oc}$  along continuous mudstone layers. In addition, a detailed characterization of the rock cores is used to correlate  $f_{oc}$  with characteristics of the depositional conditions associated with mudstone layers.

## 2. Naval Air Warfare Center

The NAWC is a 0.24 km<sup>2</sup> facility in West Trenton, NJ (Fig. 1) that served as a testing facility for aircraft engines. The use of TCE at the facility resulted in releases that were later detected in the groundwater. Lacombe (2000, 2011) provides details of the source areas of TCE contamination and the subsequent remedial groundwater treatments. The NAWC is underlain by Triassic-age rocks of the Newark Basin (Olsen et al., 1996). A fault zone at the southern extent of the NAWC demarks the contact between the Stockton and Lockatong Formations (Fig. 1); however, TCE has only been detected in the Lockatong Formation underlying the NAWC (Lacombe, 2000).

The Lockatong Formation is classified as a mudstone that is characterized by cyclical transgressive and regressive marine floor conditions during deposition (Olsen et al., 1996, Lacombe and Burton, 2010). Four different rock types are discernable as mudstone layers. These rock types include light gray massive (GRY-MAS) and reddish massive (RED-

MAS) mudstone that do not exhibit layering, dark gray laminated (GRY-LAM) mudstone, and black, carbon-rich, fissile (BLK-FIS) mudstone (Lacombe, 2000, Lacombe and Burton, 2010). The GRY-MAS and RED-MAS mudstone are products of shallow water deposition, whereas the BLK-FIS mudstone is attributed to deep water depositional conditions, and the GRY-LAM mudstone is associated with depositional conditions that transition between shallow and deep water. The different mudstone layers are areally continuous and can be correlated between boreholes separated by distances over 100 m (Lacombe, 2000, Lacombe and Burton, 2010). The mudstone strata have an orientation striking N65°E with a dip angle of approximately 25°NW.

Hydraulically conductive bedding plane fractures are associated with the rheologically weaker BLK-FIS mudstone (Lacombe, 2000, Tiedeman et al., 2010). Weathering from land surface to depths of approximately 15 m has also induced permeability in the laminated mudstones. Permeable bedding plane partings are usually not observed in the GRY-MAS and RED-MAS mudstones; however, regional compression has created vertical jointing perpendicular to bedding. In general, vertical joints are confined within the individual strata and are less permeable than bedding plane features (Tiedeman et al., 2010).

Robinson et al. (2016) installed seven closely spaced boreholes at the NAWC, denoted as 83BR-89BR (Fig. 1) as part of an investigation using geophysical methods to track the introduction of remediation amendments in fractured rock. Continuous (0.06 m-diameter) rock core was collected in each borehole up to approximately 36 m below land surface. The core was inspected to identify the different types of mudstone as a function of depth in each borehole (Shapiro and Hayes, 2017); only the GRY-MAS, GRY-LAM, and BLK-FIS mudstones were observed in cores from 83BR-89BR; the RED-MAS mudstone occurs at greater depths at this location underlying the NAWC. Following the lithologic inspection of the rock cores, samples of rock core from 83BR-89BR were selected for analyses of  $n$  (Shapiro and Evans, 2017, Shapiro et al., 2017) and  $f_{oc}$  (Shapiro and Brenneis, 2018).

Because the presence of fractures and fissile rocks often provides poor or displaced core recovery, results of the borehole wall image logs were used to correct the depths of rock core collected during coring. The depths of rock samples were corrected by correlating features observed in the optical televiewer images of the borehole wall with similar features observed in the core. Natural gamma logs were used to correct for the dip of the sedimentary bedding to compare rock properties between adjacent boreholes. The geophysical logs for boreholes 83BR-89BR are available from the U.S. Geological Survey (USGS) web application USGS GeoLog Locator (<https://webapps.usgs.gov/GeoLogLocator/#/>).

## 3. Variability of $f_{oc}$

In total, 378 samples of rock core from the seven boreholes were selected for analyses of the total carbon fraction ( $f_c$ ) and  $f_{oc}$ ; analyses for  $f_c$  were conducted for comparison and as a constraint on results for  $f_{oc}$ . The details of the sample preparation, the methods of analysis, and a listing of the results for  $f_c$  and  $f_{oc}$  are given in Shapiro and Brenneis (2018). The depth in the borehole and the mudstone type associated with each rock sample are also listed.

Values of  $f_{oc}$  vary over two orders of magnitude, with a standard deviation (0.0068) approximately equal to the mean (0.0064) (Table 1). Fig. 2 shows values of  $f_{oc}$  and mudstone lithology plotted as a function of depth for each borehole, where the depths in each borehole are adjusted to account for the dip of bedding. Adjusting the elevations to account for the dipping mudstone units shows the continuity of the mudstone layers, in particular, the continuity of the BLK-FIS mudstone units at depths of approximately 25, 30 and 34 m. Weathering of the rock due to increased groundwater flow and unrecovered sections of core affect interpretations of the continuity of the BLK-FIS mudstone at depths < 20 m (Shapiro et al., 2017).

Fig. 2 also shows the largest values of  $f_{oc}$  in each borehole appear in

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