Distribution of carbonaceous matter in lithofacies: Impacts on HOC sorption nonlinearity

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ABSTRACT

Both the composition and distribution of the lithocomponents within an aquifer impact hydrophobic organic compound (HOC) transport. Using samples from the sandy, low fraction organic carbon content (f_{oc}~0.02%) Borden aquifer, we demonstrate how HOC sorption is controlled by the carbonaceous matter (CM) associated with calcareous sedimentary lithocomponents. Two-point isotherms using perchloroethene (PCE) as a sorbate showed that medium-grained lithofacies have a broader range of K_f (Freundlich coefficient), $1/n$ (Freundlich parameter) and f_{oc} than fine-grained facies. Dual-mode (linear + Freundlich) sorption modeling, fraction inorganic carbon (f_{ic}) and laboratory analyses confirm that both the magnitude and variability of PCE K_d (sorption distribution coefficient) in the Borden aquifer are controlled by the presence of heterogeneous CM in dark and very dark carbonate lithocomponents. Laboratory analyses and model results confirmed that the CM type controlling PCE sorption behavior in the Borden aquifer is in a condensed form, likely kerogen, contained within the carbonate matrix of the grains. The dark carbonate grains comprise a small proportion of the aquifer sediment ($\ll 1\%$) and are found predominantly in medium-grained lithofacies in the Borden aquifer. These results show that increased heterogeneity, HOC mass storage and sorption nonlinearity associated with medium-grained lithofacies impact HOC transport in historically contaminated sedimentary aquifers.

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1. Introduction

Predicting hydrophobic organic compound (HOC) transport in the subsurface depends on well-developed transport models that mimic both the system's hydraulic and geochemical characteristics. Aquifer properties that determine HOC retardation are more time intensive to obtain than hydraulic parameters, because both the type and the quantity of carbonaceous matter (CM) present in the system affect HOC sorption behavior. A sorption distribution coefficient can be derived from f_{oc} and K_{oc}, where the K_{oc} is the organic carbon–water partitioning coefficient estimated from literature values and the f_{oc} is the fraction organic carbon content. Methods that assume an equilibrium partitioning coefficient

(K_d) to be linearly derived are only appropriate for situations where solute concentrations are close to solubility. These conditions may not apply in the case of plume transport (Allen-King et al., 2002). If samples exhibit sorption nonlinearity, literature K_{oc} values may significantly underestimate the amount of sorbate retardation, which impacts mass storage, transport, and remediation efficacy.

The sorption distribution coefficient ($K_{d,C}$) determined at a given concentration (denoted by subscript C) can be calculated using the following relation:

$$K_{d,C} = \frac{C_s}{C_e} \tag{1}$$

where $K_{d,C}$ (L/kg) is the sorption coefficient determined at aqueous concentration C, C_e is the equilibrium contaminant concentration in water (µg/L) and C_s is the concentration of

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contaminant sorbed to the sediment (μg/kg). In this manuscript we explore the impact on $K_{d,C}$ by grain-scale geochemical heterogeneities.

Using a geologically realistic framework (such as lithofacies) provides adequately detailed information for retarded solute transport (Allen-King et al., 1998). In this context, we are defining lithofacies in the scale of plume transport within an aquifer. A facies approach is dependent upon the characterization of lithocomponents and understanding depositional processes which contribute to grain-scale heterogeneities within lithofacies. The distribution of lithic fragments or lithocomponents within an aquifer impacts sorption magnitude and nonlinearity (Allen-King et al., 1998; Ball and Roberts, 1991a; Weber et al., 1992). Multiple samples taken from within a facies are expected to behave similarly (Grathwohl and Kleineidam, 1995). Within a facies, the composition of lithic fragments may remain the same (chemofacies), but depositional and tractional transport mechanisms will distribute lithic fragments unevenly — leading to not only poorly sorted material, but physical and geochemical spatial heterogeneities in bedding formations. Depositional heterogeneity arises due to the greater amounts of energy required in the system to transport heavier and more dense materials; and to the subsequent scouring, mixing and deposition of further sediments associated with high-energy events. Soft grains become eroded and small grains are deposited in well-sorted zones more homogeneously than larger or more resilient grains. As a result, there are important geochemical differences between sedimentological features dependent upon the bedding forms. Since the composition of lithocomponents within a specific facies is similar, the observed spatial heterogeneity of CM within these facies is due to depositional and transport processes.

The Borden aquifer is a well-studied and characterized site (Divine, 2002; Mackay et al., 1986; Roberts et al., 1986). The aquifer is a glacially-associated deposit, containing lithocomponents comprising Middle to Upper Ordovician marine carbonates (Burwasser and Cairns, 1974). Glacial deposits of this nature are quite common across North America and have some shared characteristics (sandy aquifer with overall low f_{oc}, sedimentary lithic fragments) with locations in Northern Europe (Kleineidam et al., 1999c) and Australia (Benker et al., 1998). In glacial deposits studied in North America and Northern Europe, dark carbonate lithocomponents from local source rocks (within the same geological setting) have a higher sorption capacity and affinity for HOC sorbates than the sample average (Weber et al., 1992) and/or their light-colored counterparts (Kleineidam et al., 1999a, 1999b; Weber et al., 1992). These light and dark carbonate rock fragments are uplifted marine rocks that have undergone diagenesis and contain condensed, highly sorptive CM to which the nonlinear sorption has been ascribed (Kleineidam et al., 1999c). We suspect that lithofacies containing granular material (>2 mm) will have greater and more variable sorption nonlinearity, and that this will be directly attributable to lithocomponent type.

Early work determined that HOC sorption in Borden sediment is nonlinear, and that coefficients of sorption normalized to organic carbon (K_{oc}) are greater than estimated K_{oc} values derived from the aqueous solubility of the compound using a linear free energy relationship (LFER) (Ball and Roberts, 1991a; Curtis et al., 1986). LFER approaches have limitations if there are dominant adsorptive processes or site-specific conditions. Subsequent investigations of the relations between sorption and various types of CM (kerogen, char, etc.) in Borden identified a highly-adsorptive, condensed, glassy carbon phase found within unconsolidated bulk Borden sediments (Allen-King et al., 2006; Ran et al., 2005). Further work on magnitude and variance are emphasized in another study (Divine, 2002), part of which was used to select samples for this study.

The scope of this study was to evaluate K_d nonlinearity exhibited by lithofacies (at Borden Ontario, Canada) containing carbonate granular material, compared to lithofacies without. The effects of this highly sorptive CM, its association with carbonate lithic fragments, and its distribution within the Borden sediments as related to lithofacies are not well understood. Greater K_d variance was associated with medium-grained lithofacies compared to fine-grained lithofacies (Divine, 2002). Differences between high-sorbing samples to low-sorbing samples should be demonstrably related to the distribution of lithocomponents, and the variety of CM contained within. Differences in sorption nonlinearity within a unit are then attributed to lithocomponent proportional differences (i.e., more light sedimentary vs. dark sedimentary in a given sample). Well-sorted, fine-grained lithofacies should exhibit less difference in nonlinear behavior between high-sorbing to low-sorbing fractions than medium-grained lithofacies, as lithocomponent distribution should be more homogeneous within a defined unit. We posit that variation in nonlinear K_{oc} will be associated with medium-grained lithofacies, demonstrating that carbonaceous matter heterogeneity is associated with lithocomponent proportions.

Elucidating causal compositional differences and nonlinearity by facies can provide insight into the macrokinetic and enhanced spreading behaviors observed for HOCs from the Stanford–Waterloo tracer experiment (Allen-King et al., 2006; Miralles-Wilhelm and Gelhar, 1996; Roberts et al., 1986). Sorption nonlinearity and higher sorption magnitudes have been associated specifically with carbonate lithic fragments, and this behavior has been found with Borden material (Allen-King et al., 1998; Ball and Roberts, 1991a, 1991b). The association between inorganic carbon and K_d magnitude was previously noted by Ball and Roberts (1991a); it was suspected that the carbonaceous matter contained within carbonate granules played a significant role in sorption behavior, and therefore the contribution to sorption from carbonate grains required further investigation. Limited study has been made on the impacts of lithofacies containing granular material on sorption nonlinearity with changing solute aqueous concentrations.

In this study, we compared sorption in five of eleven previously-identified lithofacies from the Borden tracer test study site in Borden, Ontario (Divine, 2002), one sample consisting entirely of granules, and four granular lithocomponent samples. Based on previously-derived K_d cumulative distribution functions (Divine, 2002), we selected samples that were expected to be highly sorbing (ones of types found above the 80th percentile of the cumulative distribution), and ones that were expected to be low sorbing (of the type found below the 20th percentile of the cumulative distribution). The granule sample and mixed bulk aquifer sample were compared for K_d, f_{oc} and f_{ic} (fraction of inorganic