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Effect of polydispersity on natural organic matter transport

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ABSTRACT

The mobility of humic-substance dominated natural organic matter (NOM) concentrated from a freshwater wetland by reverse osmosis was examined in sand columns at pH 5–8, in 0.001 M and 0.01 M $NaClO_4$. Greater mobility was observed at higher pH and lower ionic strength, although breakthrough curves (BTCs) for bulk NOM exhibited extensive tailing under all conditions examined. Based on observations from previous batch experiments indicating preferential adsorption of intermediate to high molecular weight (MW) NOM, we postulate that 'adsorptive fractionation' of the NOM pool leads to the observed tailing behavior, and develop a novel approach to assess the effects of polydispersity on transport of NOM and associated contaminants. BTCs for different NOM fractions were constructed by separating column effluent MW distributions determined by high-pressure size exclusion chromatography into five discrete intervals or 'bins' and calculating the mass of NOM within each bin at four sampling times. Observed retardation factors (R_o), reflecting median arrival time relative to that of a nonreactive tracer, ranged from 1.4 to 7.9 for the various bins and generally increased with MW. NOM retarded transport of the contaminant metal Cd (2.5 ppm, in 0.01 M $NaClO_4$) slightly at pH 5 and more substantially at pH 8. Although Cd had little or no effect on bulk NOM transport, retention of the more aromatic, IMW-HMW NOM appeared to be slightly enhanced by Cd. Study results demonstrate that heterogeneity in retardation as a function of MW is likely a major factor contributing to bulk NOM BTC tailing and may have important implications for contaminant transport.

1. Introduction

Natural organic matter (NOM) is ubiquitous in aquatic and terrestrial environments and influences transport of heavy metals (Bryan et al., 2005), radionuclides (McCarthy et al., 1998), and hydrophobic organic contaminants (Johnson and Amy, 1995). A quantitative understanding of NOM transport is thus essential for assessing potential contaminant mobility. Yet because NOM is a polydisperse mixture of molecules with a wide range of molecular weights (MWs), chemical compositions, and functional group identities and distributions (Aiken et al., 1985; Cabaniss et al., 2000), modeling of NOM transport is challenging.

NOM subsurface transport is controlled at least in part by sorption to the porous medium, which is influenced by such factors as: (1) mineral surface properties, (2) flow rate, (3) solution conditions such as NOM concentration, pH, ionic strength (I), and concentrations of multi-valent cations, and (4) the physicochemical characteristics of the NOM itself (e.g., Tipping, 1981; Vermeer et al., 1998; Avena and Koopal, 1999;

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Namjesnik-Dejanovic et al., 2000; Zhou et al., 2001; Hur and Schlautman, 2003; Maurice et al., 2004; Weng et al., 2006; Maurice, 2009). The various components of NOM display a range of adsorption rates and affinities as determined largely by MW (e.g., Meier et al., 1999; Namjesnik-Dejanovic et al., 2000; Cabaniss et al., 2000; Zhou et al., 2001; Hur and Schlautman, 2003), although other factors (at least some of which often correlate with MW) including aromaticity, carboxyl group content, and amino acid residues can also be important (McKnight et al., 1992). Preferential adsorption of intermediate to high MW components can lead to different average properties of NOM in the dissolved versus adsorbed phases (e.g., Meier et al., 1999; Namjesnik-Dejanovic et al., 2000; Zhou et al., 2001; Hur and Schlautman, 2003; Pullin et al., 2004), a process often termed 'adsorptive fractionation' (McKnight et al., 1992). Adsorptive fractionation can involve both kinetic and thermodynamic (stability) effects; for example, Zhou et al. (2001) observed in batch studies of fulvic acid adsorption on goethite that lower MW (LMW) components adsorbed quickly but were gradually replaced by intermediate to higher MW (IMW-HMW) components. This has important implications for contaminant mobility because various NOM components differ in their abilities to bind and transport contaminants (Cabaniss et al., 2000).

In both column experiments and field studies, breakthrough curves (BTCs) for bulk NOM are characterized by an initial steep rise followed by extensive tailing, suggesting rapid breakthrough of certain NOM components followed by slow breakthrough of others (e.g., Dunnivant et al., 1992; McCarthy et al., 1996). BTCs with such extensive tailing cannot be fit by the classical advection dispersion equation (ADE) – the 'textbook' standard for solute transport in saturated porous media – which assumes linear, equilibrium adsorption of a single solute. A variety of modifications can be made to the ADE to model NOM BTC tailing; to date, most efforts have focused on the effects of heterogeneous adsorption kinetics using parameters determined from batch experiments. One approach treats NOM as an essentially homogeneous solute and accounts for adsorption heterogeneity by postulating two different types of adsorption sites with fast versus slow kinetics (Jardine et al., 1992; Dunnivant et al., 1992; McCarthy et al., 1993, 1996). In another approach (e.g., van de Weerd et al., 1999, 2002), the porous medium is modeled with a single type of adsorption site, and competitive adsorption parameters calculated for several NOM fractions are incorporated into a transport code.

Here, we demonstrate an alternative approach to assess whether BTC tailing may arise from heterogeneity in the adsorption affinities of different NOM MW intervals. Column experiments were conducted using a naturally Fe- and Al-oxide coated quartz sand and an NOM sample previously shown to undergo adsorptive fractionation to goethite (α-FeOOH) in batch experiments (Pullin et al., 2004). Transport was investigated at pH 5–8 in 0.001 M and 0.01 M $NaClO_4$. NOM MW distributions of column influent and of effluent at various times were measured and the transport rates of each MW interval calculated directly from resulting data. The primary objective of this study was to quantify the mobilities of different NOM fractions over a range of experimental conditions and thus determine whether BTC tailing might result, at least in part, from NOM polydispersity. A secondary objective was to determine the effects of NOM and of the contaminant metal Cd(II) on one another's mobility.

2. Materials & methods

2.1. Natural organic matter

NOM was concentrated on-site from surface water at Nelson's Creek, a first-order stream in the Ottawa National Forest (MI, USA), using a portable RealSoft PROS/1S reverse osmosis (RO) system (Sun et al., 1995). The physicochemical properties of the RO concentrate and of raw filtered water collected simultaneously were compared by Pullin et al. (2004) and are summarized in Table S1 in the supplementary data (SD). The weight and number average molecular weights (M_w and M_n, respectively) are higher for the RO concentrate than for the bulk water, likely reflecting removal of low molecular weight components and/or potential condensation or coagulation on the RO membranes as suggested by Maurice et al. (2002). Although the values of M_w, M_n, and the polydispersity (ρ) are consistent with those of aquatic fulvic acids (e.g., Chin et al., 1994), we use the more general term NOM because the humic fractions are strictly (operationally) defined by XAD resin isolation (Aiken et al., 1985).

2.2. Geosorbent

Columns were packed with naturally Fe/Al-oxide coated quartz sand from the U.S. Department of Energy research site in Oyster, Virginia (hereafter referred to as the Oyster sand). Characteristics of this sand are described by Dong et al. (2002) and in the SD. This geosorbent was chosen because many quartz sands contain coatings that enhance NOM adsorption relative to that of 'pure' quartz surfaces (e.g., Chi and Amy, 2004; Wei et al., 2010). The sand was dry sieved with a 20–40 mesh sieve (0.842–0.420 mm), rinsed repeatedly with distilled, deionized water (DDI), and dried overnight at 55 °C. Because the sand did not contain internal porosity, we shall refer to NOM sorption as 'adsorption' and assume no 'absorption.'

2.3. Column experiments

The limited supply of NOM constrained the column size, number and breadth of experiments, and number of replicate experiments. Columns consisted of a borosilicate glass barrel 10 cm long with 1.0 cm inner diameter (Kimble–Kontes; Vineland, NJ) and were rinsed repeatedly with DDI water, then acetone, and dried at 60 °C prior to each use. Columns were wet packed by filling with background electrolyte and slowly adding sand grains while tapping gently to remove air bubbles. Porosity was calculated from column weight under dry versus saturated conditions. A gravity-feed system passed solutions through the stationary sand grains at a constant flow rate of ~2 mL/min. From 20–25 mL (~6–7 pore volumes) of background electrolyte was passed through the column prior to introducing the experimental solution. All column experiments were repeated in duplicate.