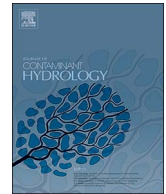




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Transport of dissolved organic matter in Boom Clay: Size effects

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ABSTRACT

A coupled experimental-modelling approach was developed to evaluate the effects of molecular weight (MW) of dissolved organic matter (DOM) on its transport through intact Boom Clay (BC) samples. Natural DOM was sampled *in-situ* in the BC layer. Transport was investigated with percolation experiments on 1.5 cm BC samples by measuring the outflow MW distribution (MWD) by size exclusion chromatography (SEC). A one-dimensional reactive transport model was developed to account for retardation, diffusion and entrapment (attachment and/or straining) of DOM. These parameters were determined along the MWD by implementing a discretisation of DOM into several MW points and modelling the breakthrough of each point. The pore throat diameter of BC was determined as 6.6–7.6 nm. Below this critical size, transport of DOM is MW dependent and two major types of transport were identified. Below MW of 2 kDa, DOM was neither strongly trapped nor strongly retarded. This fraction had an averaged capacity factor of 1.19 ± 0.24 and an apparent dispersion coefficient ranging from 7.5×10^{-11} to 1.7×10^{-11} m²/s with increasing MW. DOM with MW > 2 kDa was affected by both retardation and straining that increased significantly with increasing MW while apparent dispersion coefficients decreased. Values ranging from 1.36 to 19.6 were determined for the capacity factor and 3.2×10^{-11} to 1.0×10^{-11} m²/s for the apparent dispersion coefficient for species with $2.2 \text{ kDa} < \text{MW} < 9.3 \text{ kDa}$. Straining resulted in an immobilisation of in average $49 \pm 6\%$ of the injected 9.3 kDa species. Our findings show that an accurate description of DOM transport requires the consideration of the size effects.

1. Introduction

Natural organic matter is present in soils and sediments as solid, particulate or dissolved species. Dissolved Organic Matter (DOM) is assumed to correspond to the fraction of organic carbon that is smaller than 0.45 μm (Zsolnay, 1996; Zsolnay, 2003). Because of its size range, up to 0.45 μm , the dissolved fraction of OM, as defined in this work, includes both solutes and colloids. DOM in pore water influences the transport of contaminants such as heavy metals (Kalmykova et al., 2010; Paradelo et al., 2012), hydrophobic organic compounds (Kögel-Knabner and Totsche, 1998; Sojitra et al., 1996) or radionuclides (Maes et al., 2011; Maes et al., 2006; Mibus et al., 2007; Warwick et al., 2000). Its role in contaminant transport is linked to: 1/its capacity to bind contaminants, 2/ its capacity to interact with minerals and solid OM and 3/its mobility through soils and sediments. The last two factors depend on the pore water chemistry (Feng et al., 2005; Shen, 1999; Weng et al., 2007), the composition of soils and sediments (Kahle et al., 2004; Kaiser and Guggenberger, 2000; Kaiser et al., 1996), their pore size distribution (Put et al., 1998; Tiemeyer et al., 2017) and on the physicochemical properties of DOM itself (Weng et al., 2006; Weng et al., 2002; Zhou et al., 2001). Several batch and column experiments

showed a relation between molecular weight (MW) and/or size of the DOM species and their interaction with minerals (Seders Dietrich et al., 2013; Van de Weerd et al., 1999; Van de Weerd et al., 2002). The adsorptive fractionation favours sorption of larger organic species containing more aromatic structures (Meier et al., 1999; Namjesnik-Dejanovic et al., 2000; Zhou et al., 2001). In parallel, in clay-rich environment such as those intended for deep geological nuclear waste disposal, some studies reported the role of colloid size on their mobility. Though they did not work directly on DOM, Alonso et al. (2011) investigated the diffusion of gold colloids in the consolidated Callovo-Oxfordian and Opalinus clays and in compacted bentonite. They showed that because of a reduction of accessible porosity, the larger colloids displayed lower diffusion coefficients. Similar observations were made by Reszat and Hendry (2009) on a clay-rich aquitard, though their measured diffusion coefficients for natural organic matter and polymers were substantially higher than for the colloids used by Alonso et al. (2011). Put et al. (1998) observed a decrease in the recovery of DOM transported through Boom Clay samples with the increase of MW as well as a higher retardation for the largest species.

Despite these observations on the role of DOM MW and size, most studies on DOM transport or DOM-facilitated transport of contaminants

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use a single set of transport parameters representative of an ‘average’ behaviour of all DOM species. Martens et al. (2010) modelled the *in situ* transport of C14-radiolabelled OM in Boom Clay via several approaches considering linear/non-linear sorption or colloid attachment/detachment but lumped DOM MWD into a single species. Maes et al. (2011) who investigated the role of DOM in radionuclide transport followed the same approach. To integrate the influence of DOM heterogeneity on its transport behaviour, Van de Weerd et al. (2002) proposed a model in which OM is described as a mixture of fractions that vary in their adsorption/desorption behaviour while competing for the same sites. However, the authors did not consider any physical constraints applied on the DOM fractions during transport. Within the EU TRANCOM-CLAY project, a model attributing a velocity distribution to DOM was used to account for size effects on the transport of DOM through Boom Clay (Trancom-Clay, 2000). This approach gave some nice results for the small species but failed somewhat for the high MW species notably because it did not include size effects on the retardation of DOM.

Understanding the transport processes and quantifying the transport parameters of DOM along its MW distribution (MWD) is essential to assess contaminant dispersion especially in clay-formations in which small pores will constrain the colloid mobility by straining process. Straining is the trapping of colloid particles in down gradient pore throats that are too small to allow particle passage (Bradford et al., 2003). In other words, straining occurs when colloids are retained in pores that are smaller than some critical size. Complete straining, *i.e.* total immobilisation, can be associated to a pore throat diameter of the solid that is a combination of pore size distribution, pore space geometry and pore connectivity. A detail assessment of DOM mobility and more generally of colloid mobility requires the determination of 1/ pore throat diameter of the porous medium and 2/ the transport parameters of the species smaller than the pore throat diameter that can be limited by physical (straining) and/or chemical reaction (attachment).

The objective of this research is to develop a coupled experimental-modelling approach to assess the pore throat diameter and the transport parameters of DOM in Boom Clay. Boom Clay is studied as a potential host rock for nuclear waste repository in Belgium. Up to 270 mgC/L are found in the pore water (Durce et al., 2015) and assessing the transport of DOM is essential for safety assessment. Yet, due to Boom Clay DOM heterogeneity and polydispersity, an experimental determination of DOM transport parameters is challenging. In their work on transport of DOM through Al/Fe-coated quartz sand, Seders Dietrich et al. (2013) used size exclusion chromatography (SEC) to discretise DOM MW fractions and evaluate their respective retardation in column experiments. We extend this approach by coupling percolation experiments and SEC measurements to a 1D reactive transport model to determine the retardation, diffusion and immobilisation such as attachment or straining processes of DOM. In our approach, DOM is a mixture of species with different MW and a discretisation of the whole DOM pool into several species is made using the SEC MWD. The extracted breakthrough curve of each individual species is then modelled.

2. Material and methods

2.1. DOM sample

In this work we used natural DOM present in the Boom Clay pore water. The pore water was sampled from the EG/BS piezometer (S-1D) installed in the HADES underground research facility (Mol, Belgium). This piezometer contains one stainless steel cylindrical filter screen which is integrated in a coarse sand column of 13 m long hydraulically interconnecting the pore water from -247 m to -260 m BSL of the Boom Formation. DOM in this pore water displays a broad MWD ranging from species of few hundred Da to aggregates larger than 100 kDa (Durce et al., 2015). The polydispersity of the sample permits to study the transport properties of DOM over a large range of MW.

The sample of EG/BS pore water contains 161 ± 2 mgC/L of

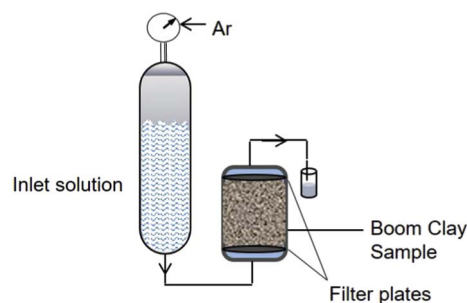


Fig. 1. Scheme of the percolation set-up.

dissolved organic carbon measured after filtration at $0.45 \mu\text{m}$ (VWR, PVDF) on a carbon analyser IL 550 TOC TN (HACH LANGE). The corresponding UV absorbance at 280 nm, used further as the reference detection wavelength, was measured on a UV-Vis Lambda 40 spectrophotometer (Perkin Elmer) at $4.73 \pm 0.06 \text{ cm}^{-1}$. The MWD of DOM in the EG/BS solution (Fig. 2) was determined by SEC according to the protocol described later in section 2.3. The pH of the EG/BS solution was measured at 8.3. The ionic composition of the sample was not determined in this work but Boom Clay pore water is of sodium bicarbonate type with a typical composition of $\sim 0.015 \text{ M NaHCO}_3$. For more details on the exact composition of EG/BS pore water, we refer the reader to the data reported by Durce et al. (2015).

2.2. Transport experiments

The transport of DOM through Boom Clay was investigated in laboratory percolation experiments. The Boom Clay plugs were placed in a stainless steel cell in between two filter plates. The inlet solution referred to as the percolation solution is pressurized with Ar and percolated through the Boom Clay plugs with a fixed pressure gradient. Fig. 1 displays a schematic overview of the percolation set-up.

Two percolation experiments were performed: one with a pressure gradient of 8 bars and one of 18 bars, further referred as P8 and P18, respectively. A Boom Clay sample was cored in the HADES underground facility (Mol, Belgium) making use of a stainless steel cutting edge and was conserved at 4°C in its original sealed cutting edge until use (to prevent dehydration and oxidation). The clay sample was then extruded from the cutting edge, cut into two plugs of dimensions $\sim 38 \times 15 \text{ mm}$ ($\varnothing_{\text{plug}} \times L_{\text{plug}}$) and further introduced in the stainless steel cells such as the flow was perpendicular to the bedding. Table 1 reports the origin of the sample and the exact dimensions of the plugs. The mineralogical composition of the Boom Clay sample is reported in the Electronic Supplement.

The Boom Clay plugs were first pre-equilibrated using Synthetic Boom Clay Water as inlet solution to leach out the background of indigenous mobile DOM. The synthetic pore water is used as a proxy of the reference pore water but without natural DOM. More details on its preparation and composition are given in Durce et al. (2015). To follow the equilibration, the outlet solutions were sampled regularly and the absorbance at 280 nm (Lambda 40 spectrophotometer, Perkin Elmer) was measured. The BC plugs were assumed ‘equilibrated’ when the absorbance of the outlet solution was negligible.

Filtered EG/BS pore water ($0.45 \mu\text{m}$, PVDF, VWR) was then introduced in the inlet reservoirs and percolated through the clay plugs. The outlet solutions were collected regularly and analysed by UV-Vis spectroscopy at 280 nm and by SEC (section 2.3) to follow the breakthrough of mobile DOM. A total volume of 375.8 mL (442 days) and 565.3 mL (441 days) of EG/BS were percolated in experiments P8 and P18, respectively. Outlet flow rates were measured by weighing the outlet solutions.

Breakthrough curves are plotted as the normalized instantaneous absorbance at 280 nm ($\text{UV280}/\text{UV280}_0$) extrapolated from SEC results

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