Supporting Information

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ONE DIMENSIONAL DIFFUSIVE FLUX EQUATIONS

One-dimensional diffusive flux of solutes or colloids, i, through a porous medium can be described by Fick's first law of diffusion,

$$J_D^i = -D_e^i n_e^i \frac{\partial C^i}{\partial x}$$
[S1]

where D_e^i is the effective diffusion coefficient, n_e^i is the effective porosity, and $\partial C^i / \partial x$ is the concentration gradient of *i*. The definition of D_e is not consistent within the literature (Shackelford, C. D. Laboratory diffusion testing for waste disposal – A review. J. Contam. Hydrol. 1991, 7, 177–217). In some cases, n_e is incorporated within D_e . Here we define D_e according to Eqn. [S1]. The diffusion of *i* in a porous medium is different than in free water (D_e^i) because diffusion is affected by the length of the diffusion path, or tortuosity (τ^i) , for each constituent. Thus the D_e^i in a porous media is less than the D_o^i and can be determined using,

$$D_e^i = \tau^i D_o^i$$
[S2]

Tortuosity can be expressed by the application of the Hagen-Poiseuille equation,

$$\tau^{i} = \left(\frac{l}{l_{e}}\right)^{2}$$
[S3]

where *l* is the straight line distance between two points, and l_e is the actual distance of transport through the porous media. In our experiment, both D_e^i and D_o^i were determined experimentally, and as a result we could estimate τ^i .

The one-dimensional diffusion equation for a porous medium, according to Fick's second law, is:

$$\frac{\partial C}{\partial t} = \frac{D_e^i}{R_d^i} \frac{\partial^2 C}{\partial x^2}$$
[S4]

where *C* is the concentration of solutes or colloids in solution, *t* is the time, *x* is the distance, and R_d^i is the retardation factor.

BATCH SORPTION TESTING

Subsamples of core from 11.5–12.0 m BG were oven dried at 80°C and subjected to batch testing using a 1:4 soil to water ratio (3 g soil to 12 g solution) to determine the degree of sorption of colloidal materials onto the till. The extent of sorption of colloidal material (PSS 910, PSS 1430, PSS 4800, PSS 6500, PSS 15450, SRHA, SRFA) was examined by creating solutions of 11.7 m BG pore water (in equilibrium with core material) with a range in colloid concentrations (5–300 mg L^{-1}). To determine sorption of the naturally occurring DOC to the till, pore waters from 2.2, 3.7, 6.9, 9.7, and 11.7 m BG (with a range in DOC concentrations from 30 to 145 mg L^{-1} ; described below) were mixed at 1:4 soil water ratio with the solids collected from 11.5–12 m BG. The soil-water mixtures were agitated on a wrist action shaker for 48 h. After the soil settled in the mixtures (about 1 h), the supernatant was collected and filtered through 0.45 μ m filters. This approach was used to minimize the potential for settlement of colloids during centrifugation. Colloid concentrations remaining in solution were measured using area units from AsFIFFF runs. Each sample was run in triplicate and results averaged. The areas determined from the AsFIFFF were then recalculated as concentrations, and plotted as C vs. S, where C is the concentration of colloid in solution in equilibrium with the mass of colloid sorbed onto the clay (mg L^{-1}) and S is the mass of

colloid sorbed per dry unit weight of solid (mg kg⁻¹). The resulting plot was used to determine the distribution coefficient K_d^i (mL g⁻¹) using

$$S = K_d^i C$$
[S5]

Because the sorption plots were linear (data presented in main document), a linear sorption isotherm was used to determine the retardation factor (R_d^i). Specifically,

$$R_d^i = 1 + \frac{\rho_{bulk}}{n_e^i} K_d^i$$
[S6]

where ρ_{bulk} is the bulk density of the porous media (g cm⁻³), K_d^i is solid-solution distribution ratio, with units of (massⁱ/mass_{bulk})(volume_{solution}/massⁱ) (mL g⁻¹), and n_e^i is the effective porosity of the tills with respect to each colloid. A ρ_{bulk} of 2.17 g cm⁻³ was used in these calculations and n_e^i was determined 1D diffusion modeling of the diffusion cell test results (described in text).

COLLIOD CHARACTERIZATION

Characterization of the concentration, M_w , hydrodynamic diameter (D_H) and aqueous diffusion coefficient (D_o^i) of the colloids collected from the diffusion cells and batch experiments was conducted using an AsFIFFF system which allowed individual colloids to be identified as separate peaks. The integration of each peak (area) was linearly related to its concentration, with an r² value of not less than 0.99 (data not presented). Each sample was run in duplicate. The difference in integrated peak areas between duplicate samples ranged from a minimum of 0.58%, a maximum of 22.1%, and an average of 8.5% for all samples run. This approach allowed us to differentiate natural DOC contained within pore water samples from the other colloids, as well as measure changes in all colloidal concentrations in the batch and diffusion cell experiments. The PC controlled AsFIFFF system consisted of an arrangement of pumps, an AsFIFFF channel, and a vacuum degasser (to remove air bubbles from the carrier solution that may interfere with separation efficiency in the AsFIFFF channel). The AsFIFFF system primarily separates colloids by differences in aqueous diffusion coefficients (D_o^i). Colloids are detected by a UV detector (254 nm) as they elute from the system after fractionation. The resulting plots of detector intensity vs. time, called fractograms, consist of two regions: the void peak, which may contain some undifferentiated low molecular weight (M_w) ligands, and the colloidal peak(s). UV measurements were made at 1 s intervals with data acquisition software provided by Postnova Analytics (NovaFFF version 3.14). To ensure colloidal material of interest was not lost through the membrane into the cross flow during analysis, the AsFIFFF channel was fitted with regenerated cellulose acetate membranes (Millipore Corp.) with a nominal M_w cut-off of 1000 Da. A Rheodyne 100 μ L manual sample injection loop was used to inject filtered (<0.45 μ m) water samples into the AsFIFFF.

Hydrodynamic diameters (D_H) of the polymers and DOC were determined from AsFIFFF theory and the elution time of each component. The elution time of any particle separated by AsFIFFF is dependent on the experimental setup and flow rates within the channel, which affect the retention time of the colloid. The retention of a component within the channel is expressed by:

$$R = \frac{t^{o}}{t_{r}}$$
[S7]

where *R* is the retention ratio, t_r is the retention time, and t^0 is the void time. The void time of the channel is calculated from the expression,

$$t^{0} = \frac{V^{0}}{V_{c}} \ln \left(1 + \frac{V_{c}}{V_{out}} \left[1 - \frac{\omega \left(b_{0} z' - \frac{b_{0} - b_{L}}{2L} z'^{2} - y \right)}{V^{0}} \right] \right)$$
[S8]

where V_{out} is the channel outlet flow rate, z' is the distance form the inlet to the focusing point, L is the channel length, b_0 and b_L are the channel breadths at the inlet and outlet, respectively, and y is the area cut off by the tapered inlet end. To calculate the void time, the flow parameters of the channel are measured volumetrically, and the channel thickness is measured from a standard of known diffusion coefficient. In this case we used ferritin ($M_w =$ 440000). With this diffusion coefficient, the channel thickness is calculated using

$$\omega = \sqrt{\frac{D6t_r}{\ln\left(1 + \frac{V_C}{V_{out}} \left[1 - \frac{\left(b_o z' - \frac{\left(b_o - b_L\right)}{2L} z'^2 - y\right)}{A}\right]\right)}}$$
[S9]

From the retention ratio the retention parameter, λ , is determined using

$$R = 6\lambda \left[\coth\left(\frac{1}{2\lambda}\right) - 2\lambda \right]$$
 [S10]

The D_H of the fractionated particles is then calculated using

$$D_{H} = \frac{kTV^{0}}{3\pi\eta V_{C}\omega^{2}}\frac{1}{\lambda}$$
[S11]

and D_o^i is calculated using,

$$D_o^i = \frac{kT}{3\pi\eta D_H}$$
[S12]

The calculation of colloid D_H assumes spherical particles. Although valid for the poly(styrene) suphonates, this assumption remains to be verified for the DOC colloids.

POREWATER CHEMISTRY

Major cation and anion chemistry of the samples used in the diffusion experiments is presented in the following table. DOC concentrations are presented in the main document text.

Depth	pН	HCO ₃ ⁻	Ca ²⁺	Cl	Mg ²⁺	K^+	Na^+	SO4 ²⁻	NO ₃ ⁻	Fe	Mn
(m)	(units)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
2.2	7.89	681	420	68	5,500	82	8,700	39,600	3.0	0.03	0.013
3.7	7.93	742	410	69	6,600	85	9,700	46,100	0.7	0.02	0.003
6.9	8.04	946	400	37	2,900	48	4,600	20,400	1.5	0.02	1.38
9.7	7.91	924	420	71	1,270	37	2,880	11,200	0.8	0.006	1.07
11.7	7.88	889	423	165	379	30	1,590	4,800	4.5	0.008	1.07