Transport and Retention of Fullerene Nanoparticles in Saturated and Unsaturated Porous Media

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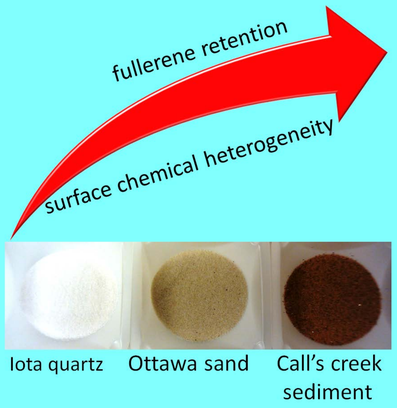
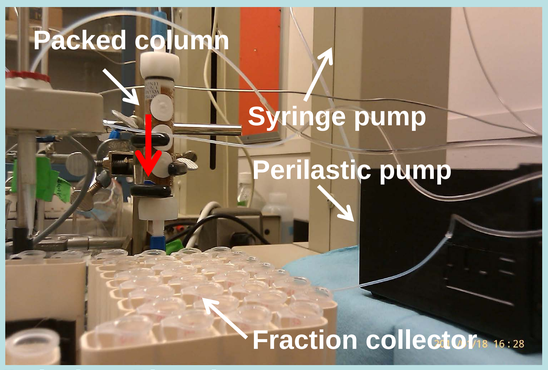
Introduction



Increasing production and use of fullerene-based nanomaterials is likely to result in their environmental dispersal and subsequent human and ecosystem exposures. A thorough understanding of fullerene transport in the subsurface is essential to assessing environmental fate of fullerenes. To date, few transport studies have used actual environmental media or fullerene derivatives.

In this study, the transport of two fullerene nanoparticles (i.e., aqueous colloidal suspensions of C_{60} [aqu/C_{60}] and more water-soluble C_{60} derivative [C_{60} pyrrolidine tris-acid]) was studied in columns packed with model porous media (Iota quartz and Ottawa sand) and a sediment from Call's creek under saturated and unsaturated steady-state flows. Fullerene retention was correlated with the degree of grain surface chemical heterogeneity manifested in amorphous Al hydroxide concentrations of the three media. Surface roughness was also responsible for the greatest fullerene retention in the sediment. As explained by the XDLVO theory, water soluble C_{60} PTA was more transported than aqu/C_{60} at near neutral pH, as results of its greater hydrophilicity and smaller particle sizes. Fullerene retention was dependent on solution pH and soil water saturation degree, and underlying mechanisms were discussed.

Experimental



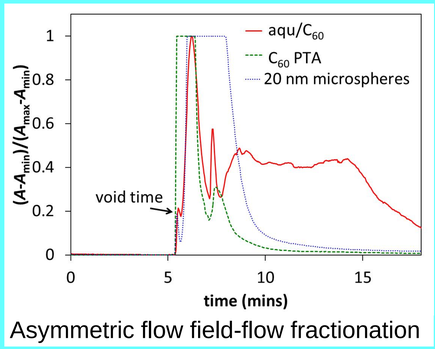
***Solution Chemistry*:**
pH 7.5 – 8.0: 0.4 mM $NaHCO_3$ + 9.6 mM NaCl
pH 4: 1.51 mM NaOAc + 10 mM AcOH
pH 10: 2.5 mM $NaHCO_3$ + 2.5 mM Na_2CO_3

***Porous Media*:** two model media & sediment

***Water Saturation* (S_w):** two levels

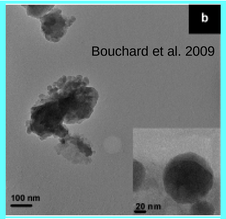
extended mixing with DI water + fullerenes → filtrations, sol. chemistry adjust. → fullerene suspensions (size & charge; toluene-water partition (k_{tw})) → **column experiments** (saturated (s_w=1); unsat. (s_w=0.57-0.66))

Fullerene Nanoparticle Size

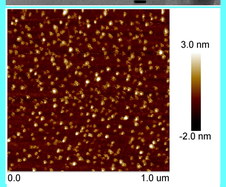


Asymmetric flow field-flow fractionation

Aqu/C_{60} TEM



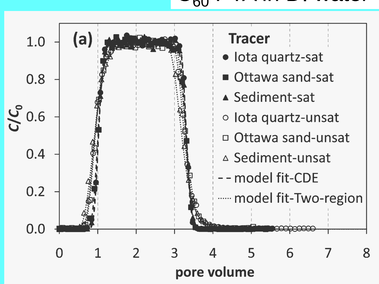
C_{60} PTA AFM

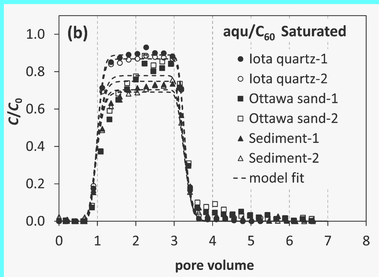


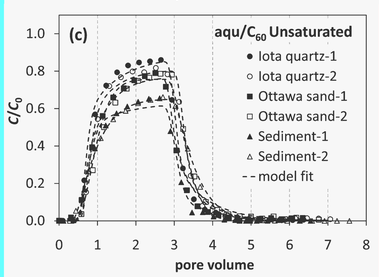
C_{60} PTA in DI water

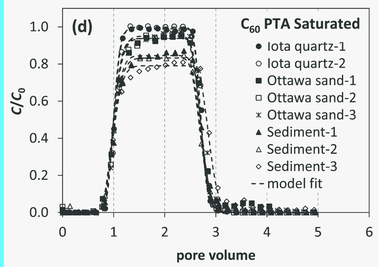
Results

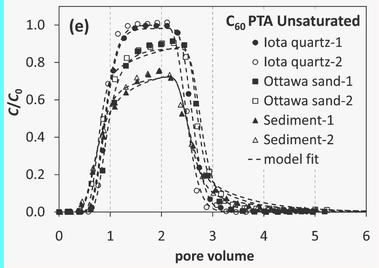
Measured and fitted breakthrough curves:
tracer (^3H_2O)
aqu/C_{60},
C_{60} pyrrolidine tris-acid (C_{60} PTA)











Modeling

Saturated media

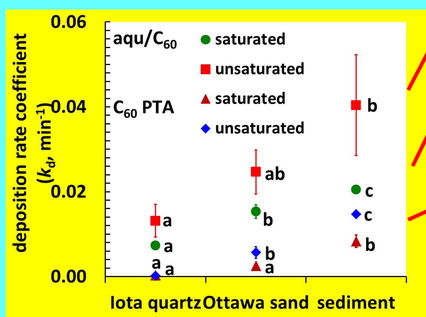
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - k_d C$$

Unsaturated media

$$\frac{\theta_m}{\theta_w}\frac{\partial C_m}{\partial t} = D\frac{\partial^2 C_m}{\partial z^2} - v\frac{\partial C_m}{\partial z} - \frac{\omega}{\theta_w}(C_m - C_{im}) - \frac{\theta_m}{\theta_w}k_d C_m$$

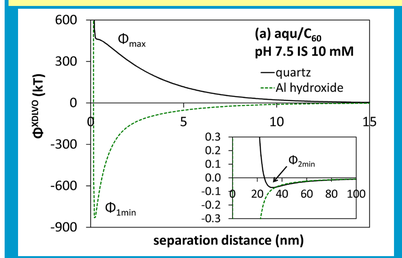
$$\theta_{im}\frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im})$$

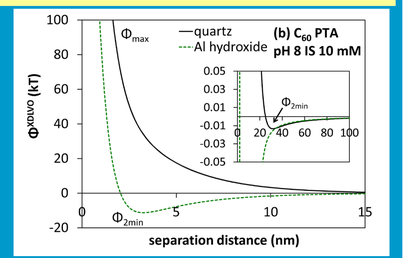
C = concentration, v = pore water velocity
D = hydrodynamic dispersion coeff.,
k_d = deposition rate coefficient
θ_m = moible water content; ω = exchange rate between two regions.

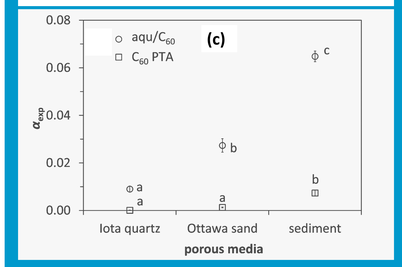


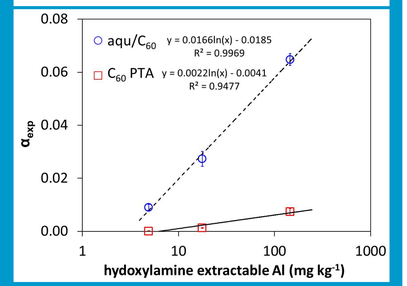
XDLVO Energies of Aqu/C_{60} & Attachment Efficiency (α)

$$\Phi^{XDLVO}(x) = \Phi^{LW}(x) + \Phi^{AB}(x) + \Phi^{EL}(x) + \Phi^{BR}(x)$$



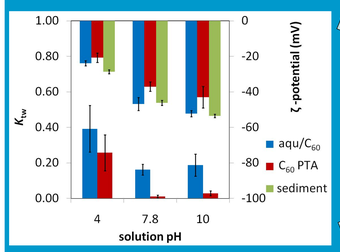






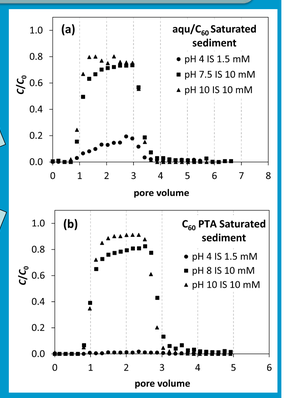
Metal oxides/hydroxides provide favorable deposition sites

pH-dependence



electrostatic

hydrophobic



Conclusions

- Fullerene retention increased with increasing grain surface chemical heterogeneity (i.e., amorphous Al oxides/hydroxides in the order of Iota quartz < Ottawa sand < sediment).
- C_{60} pyrrolidine tris-acid was less retained than aqu/C_{60} due to its hydrophilicty and smaller size at near neutral pH.
- pH dependence of fullerene retention could be partly explained by the pH-dependent surface charge of fullerene and grain surfaces, and partly by increased hydrophobicity of fullerene aggregates when solution pH approaches their isoelectric points.
- Fullerene retention was enhanced in unsaturated media, implying that fullerenes can be more attenuated in the vadose zone than in groundwater.

The main content of this presentation has previously been published in *Water Research*.
Zhang, W., C.W. Isaacson, U. Rattanaudompol, T.B. Powell, and D. Bouchard. 2012. Fullerene nanoparticles exhibit greater retention in freshwater sediment than in model porous media. *Water Res.*, 46(9), 2992-3004, doi: 10.1016/j.watres.2012.02.049.