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Influence of Montmorillonite Clay on The Transport of Organic Contaminants in Groundwater

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Abstract

Common household chemicals, such as caffeine, enter groundwater systems via wastewater. The contaminants may experience sorption and/or degradation in groundwater. These compounds are commonly used as tracers for anthropogenic contamination, making it important to understand their chemical mobility in groundwater. The role of montmorillonite on groundwater contaminant adsorption was investigated using batch experiments and saturated soil columns. Results from this study indicated adsorption of the contaminants, sulfamethoxazole, carbamazepine, and bisphenol-A, is negligible, while adsorption of caffeine can be significant depending on soil composition. For example, the retardation factor for caffeine was 190 times higher in soils containing 0.2% montmorillonite clay compared to quartz play sand without the clay. However, caffeine adsorption decreased when other three compounds were in solution, indicating the possibility of competitive adsorption influencing montmorillonite. The study also investigated whether organic chemicals adsorb to suspended nanoparticles of clay and experience facilitated adsorption or transport. Results indicate caffeine may be an unreliable tracer in the presence of clay minerals or other contaminants and that some experimental methods for determining adsorption may not be representative of real-world conditions.

1. Introduction

Common household organic chemicals including caffeine and pharmaceutical drugs enter and pass through wastewater treatment systems with negligible degradation[1,2]. As wastewater chemicals flow into the natural environment, they are transported through the vadose zone and groundwater where they may experience sorption and/or degradation depending on the chemical's nature and interaction with the soil. Contaminants will travel at the average rate of groundwater flow unless they experience sorption, which causes chemical retardation and may allow the contaminant plume to naturally attenuate before spreading[6]. Sorption may also play a role in colloid-facilitated transport, a process where chemicals sorb to colloidal clay particles in the aquifer and travel differently than a traditional aqueous contaminant[7]. A previous study found that the smectite clay, montmorillonite, has a high capacity for caffeine sorption and can be responsible for a large portion of a soil's sorption capacity at very low quantities[8]. Of several clay mineral classifications, smectite clays aid in colloid-facilitated transport the most[9] making the transport of montmorillonite in groundwater unpredictable. In order to assess wastewater contaminant transport through groundwater[10], it is important to better understand chemical sorption for modeling and monitoring purposes in the future.

In order to better quantify the sorption coefficients for wastewater contaminants to montmorillonite, batch experiments with the common[3] wastewater chemicals caffeine, sulfamethoxazole, carbamazepine, and bisphenol-A were conducted using artificial soils containing controlled concentrations of montmorillonite. Saturated soil column experiments were run with the same chemicals and controlled quartz clay mixture soils to verify the results. Columns better reflect real world groundwater contaminant transport unlike batch experiments which simply quantify sorption coefficients. In order to investigate colloid-facilitated transport influencing data, quartz saturated soil columns with various particle size were conducted as well.

2. Methods

2.1 Batch Experiments

Stock artificial soils of quartz sand and montmorillonite were created at weight percentages of 0%, 0.1%, 0.2%, 0.4%, 0.5%, and 1% clay. For each artificial soil, a series of ten individual Centrifuge vials were then filled with 10 grams of the clay-spiked soil. Each series of centrifuge vials was then injected with a solution of caffeine, sulfamethoxazole, carbamazepine, and bisphenol-A at concentrations of 100, 70, 40, 10, 8, 4, 2, 1, 0.5, and 0.2 ppm. A set of centrifuge vials at the same concentrations without soil were also created as a control. After shaking end-over-end for 24 hours, the vials were centrifuged to separate solid matter, and the supernatant was filtered with 0.45-micron nylon membranes for sample collection. Batch experiments were also conducted with only caffeine in solution (as opposed to the 4-compound mixture) using the same methodology.

2.2 Saturated Soil Column Experiments

Acrylic soil columns (350 ml) were filled with artificial soil. The soil was composed of quartz play sand and 0.2% (w/w) montmorillonite clay. Columns were dry packed and injected with deionized water at a rate of 1 ml/min for 600 minutes to flush the column and calculate porosity of the soil. The columns were then injected with an aqueous contaminant stock solution at 1 ppm with a flow rate of 1 ml/min. Samples were collected using an autosampler at time intervals appropriate for capturing the breakthrough curve of the contaminant plume based on total fluid pore volumes injected. Once the injected chemicals met an equilibrium at peak concentration the column was flushed with deionized water and the breakthrough curve was measured once again. Throughout the experiment, samples were collected from the stock solution to ensure constant initial concentrations. Samples were filtered using 0.45-micron nylon membrane. Control columns of pure quartz sand were also conducted with the same methodology.

2.3 Chemical Analysis

All samples were analyzed using gradient High-Performance Liquid Chromatography (Shimadzu Prominence HPLC modular unit) with a 75-mm C18 column and Shimadzu SPD-20A UV detector (273 nm wavelength).

2.4 Preferential Flow Tracing

Saturated soil columns were also injected with fluorescent dye tracer to investigate preferential flow. Time lapse video was taken of the columns. Once saturated with dye tracer, the soil in the columns was laid out and dissected to monitor for uninfluenced pockets of soil.

3. Results

Caffeine experienced increasing sorption to the soil as clay percentages increased from negligible sorption at 0% clay to a substantial sorption coefficients (K_d) of 5.49 L/kg at 0.1% clay to 18.74 L/kg at 1% clay (Table 1). When batch experiments were conducted with a mix of chemicals, sulfamethoxazole and carbamazepine experienced minimal sorption ($K_d < 2.03$ L/kg) while caffeine experienced similar sorption coefficients, above 5 L/kg, with all percentages of clay spiked soil (Table 2). Bisphenol-A was present in solution as well, but the data was omitted due to analytical difficulties.

Table 1. Experimental adsorption coefficients from caffeine-only batch experiments

K_d (Sorption Coefficient)	0% Clay	0.1% Clay	0.2% Clay	0.5% Clay	1% Clay
Caffeine	0.82 ±0.75	5.49 ±0.09	7.92 ±0.09	13.08 ±0.07	18.74 ±0.06

Table 2. Experimental adsorption coefficient from caffeine, sulfamethoxazole, carbamazepine, bisphenol-A mixed solution batch experiments

K_d (Sorption Coefficient)	0% Clay	0.1% Clay	0.2% Clay	0.5% Clay	1% Clay
Caffeine	0.59 ±0.20	6.05 ±0.53	5.47 ±1.01	5.06 ±0.16	5.26 ±0.16
Sulfamethoxazole	1.26 ±0.19	1.05 ±0.05	2.03 ±0.81	0.47 ±0.74	0.61 ±0.14
Carbamazepine	0.76 ±0.3	1.52 ±0.077	1.58 ±2.12	0.05 ±6.27	0.39 ±0.33

The breakthrough curve of caffeine, sulfamethoxazole, and carbamazepine exhibits a retardation factor of 1, indicating little sorption in the column while flowing through the 0% clay quartz sand control (Figure 1). Bisphenol-A was present in solution as well, but the data was omitted due to analytical difficulties.

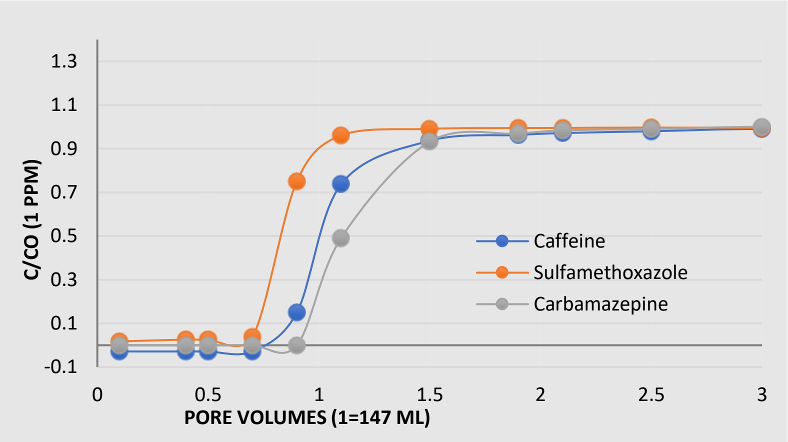

Figure 1. 0% Clay Saturated Soil Column, Control

At 0.2% (w/w) montmorillonite clay, the caffeine only breakthrough curve exhibits a retardation factor of ~30, indicating sorption is occurring within the column (Figure 2).

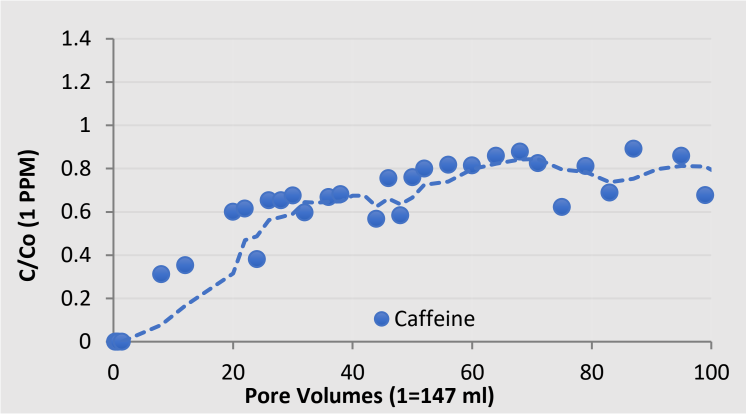

Figure 2. 0.2% Clay Saturated Soil Column, Caffeine Only

The caffeine breakthrough curve exhibited a retardation factor of 190 (465 hours), suggesting a large amount of caffeine sorption occurred while in solution with sulfamethoxazole, carbamazepine, and bisphenol-A (Figure 3). Sulfamethoxazole experienced a retardation factor of 1 exhibiting no sorption, while carbamazepine exhibited a retardation factor of 1.2. Bisphenol-A data was omitted due to analytical difficulties.

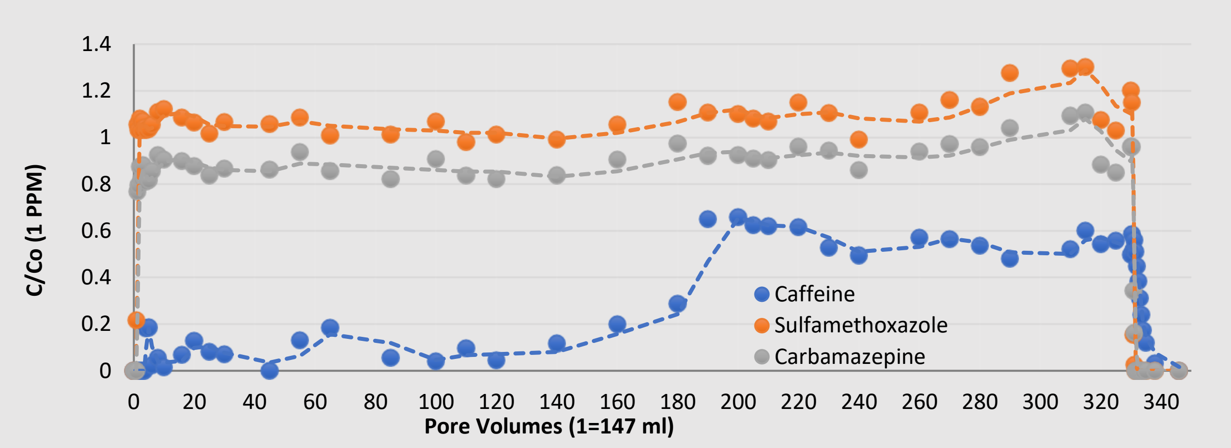

Figure 3. 0.2% Clay Saturated Soil Column, Four Chemicals in Solution

4. Discussion

4.1 Batch Experiments

In the absence of other chemicals, caffeine sorption coefficients were as high as 13.08 L/kg when montmorillonite concentrations as low as 0.5% (w/w) were present (Table 1). Once sulfamethoxazole, carbamazepine, and BPA were added to the solution, the caffeine sorption coefficient decreased to 5.06 L/kg at 0.5% (w/w) montmorillonite (Table 2). These results were unusual as caffeine is the least hydrophobic of the four compounds tested and the least likely to adsorb to soil.

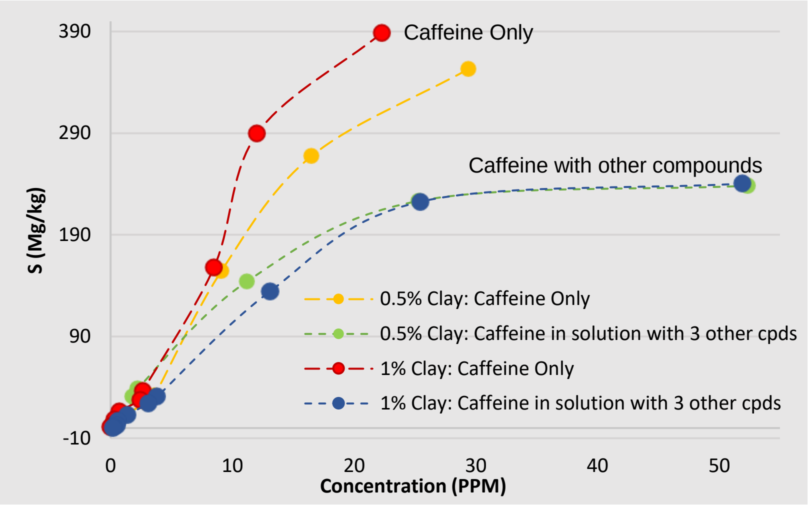

Figure 4. Adsorption isotherms of caffeine in solution compared to caffeine in solution with competing chemicals

The decrease in caffeine sorption in the presence of other chemicals in solution indicates competitive sorption to montmorillonite is occurring. It was also observed that the adsorption isotherms of caffeine are non-linear at higher concentrations and become non-linear sooner in the presence of other chemicals (Figure 4). These results imply that adsorption coefficients obtained from single chemical batch experiments may not be applicable to real-world modeling of groundwater containing multiple contaminants at a time. Given the non-linear nature of adsorption to montmorillonite, experiments conducted at high concentrations may not reflect real world chemical transport which occurs at much lower concentrations.

4.2 Saturated Soil Column Experiments

When transported through the quartz sand control column, caffeine, sulfamethoxazole and carbamazepine were shown to have a retardation factor of 1 (Figure 1); as calculated from the batch experiment with sorption coefficients of 0 L/kg using equation (1).

$$Rf \ = 1 + \left(\frac{\rho_\beta}{\eta}\right) K_d \qquad (1)$$

At 0.2% montmorillonite clay (w/w) caffeine was transported through the soil column with a retardation factor of 30 (Figure 2), similar to the predicted retardation factor of 31.7 at 0.2% clay using the batch data (Table 1) and Equation 1. Caffeine in solution with sulfamethoxazole, carbamazepine, and bisphenol-A experienced a retardation factor of 190 while transported through a 0.2% montmorillonite clay (w/w) soil column (Figure 3). This retardation greatly exceeded the predicted retardation factor of 19.2 at 0.2% clay from equation (1) and previous batch data (Table 2). Despite observing that caffeine adsorption decreased in batch experiments due to competitive sorption, the multiple compound column experiment yielded an *increased* retardation factor, showing increased adsorption instead. Potential reasons attributable to these results could be colloid-facilitated adsorption and/or preferential flow paths within the column. Testing the columns for preferential flow using dye tracer found that pockets of soil do not come in contact with flowing contaminants in heterogeneous quartz columns (Figure 5). This occurrence could be a potential source of unpredictable concentration changes and inconsistent breakthrough curves. It was also observed that despite reaching an equilibrium, caffeine never reached the original concentration of the stock solution (Figure 3). The missing caffeine is thought to be adsorbed to suspended montmorillonite particles and filtered out in sample collection.

Figure 5. Dye tracer plume traveling in the column, voids found in 0.25-0.50mm grain size columns and 1-2mm grains size columns, split cross section of two soil columns

5. Conclusion

Saturated soil column experiments show that organic chemical transport in the presence of montmorillonite may involve facilitated sorption, preferential flow paths, and nonequilibrium conditions that are not reflected in more simple calculations based on batch experiment data. Furthermore, modeling contaminant transport using adsorption coefficients obtained from batch experiments conducted with single chemicals or at high concentrations will not reflect real-world conditions. Caffeine adsorbs to minute quantities of montmorillonite that would be difficult to detect in soil using typical analytical methods. As caffeine is retarded, other wastewater chemicals such as sulfamethoxazole may travel through the groundwater uninfluenced. Using caffeine as a tracer may be unreliable and inaccurate for use in determining anthropogenic influence. Further work should be done to explore the action of caffeine-montmorillonite adsorption and potential colloid-facilitated transport.

6. Acknowledgement

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7. References

1. Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental pollution*, *163*, 287-303.
2. Conn, K. E., Barber, L. B., Brown, G. K., & Siegrist, R. L. (2006). Occurrence and fate of organic contaminants during onsite wastewater treatment. *Environmental science & technology*, *40*(23), 7358-7366.
3. Barnes, K. K., Kolpin, D. W., Furlong, E. T., Zaugg, S. D., Meyer, M. T., & Barber, L. B. (2008). A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States—I) Groundwater. *Science of the total environment*, *402*(2-3), 192-200.
4. Ferreira, A. P., de Lourdes, C., & da Cunha, N. (2005). Anthropic pollution in aquatic environment: Development of a caffeine indicator. *International journal of environmental health research*, *15*(4), 303-311.
5. Alhajjar, B. J., Chesters, G., & Harkin, J. M. (1990). Indicators of chemical pollution from septic systems. *Groundwater*, *28*(4), 559-568.
6. Abulaban, A., & Nieber, J. L. (2000). Modeling the effects of nonlinear equilibrium sorption on the transport of solute plumes in saturated heterogeneous porous media. *Advances in water resources*, *23*(8), 893-905.

7. Ryan, J. N., & Elimelech, M. (1996). Colloid mobilization and transport in groundwater. *Colloids and surfaces A: Physicochemical and engineering aspects*, *107*, 1-56.

8. Harris, J. 2013. The Role of Montmorillonite in the Removal of Caffeine from Groundwater. *University of North Carolina, Environmental Studies Department.*

9. Seta, A. K., & Karathanasis, A. D. (1997). Stability and transportability of water-dispersible soil colloids. *Soil Science Society of America Journal*, *61*(2), 604-611.

10. Sui, Q., Cao, X., Lu, S., Zhao, W., Qiu, Z., & Yu, G. 2015. Occurrence, sources and fate of pharmaceuticals and personal care products in the groundwater: a review. *Emerging Contaminants*, *1*(1), 14-24.