Project Final Report

How Carbogenic Nanoparticles (CNPs) Move Through Various Types of Porous Media Under Conditions that Replicate the Natural Environment

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Overview

Nanoparticles (NPs) used in many consumer goods, including textiles, pharmaceuticals, and water disinfectants, enter wastewater throughout the life of the product and water treatment plants do not necessarily remove them. Previous studies show that silver and zinc NPs, used as antibacterial in textiles and to disinfect water, cause significant plant biomass reduction and cell death in animals as well. Though NPs are entering drinking water supplies little research has addressed how they move through natural subsurface environments.

Many of these manufactured NPs interact with the porous medium by processes such as absorption, settling and filtration. These processes are difficult to separate out when studying flow and transport through porous media. For the work summarized within, we used recently developed carbon nanoparticles (CNPs, 5 – 10 nm in diameter) as tracers through various porous media to test their use as non-reactive tracers. These CNPs have been designed to be non-reactive, neutral buoyancy, and hydrophilic.

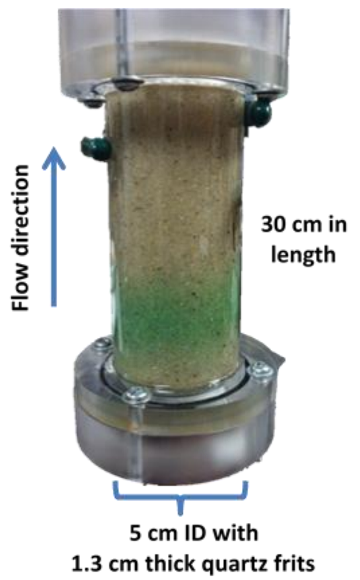
Research and Project Experiments

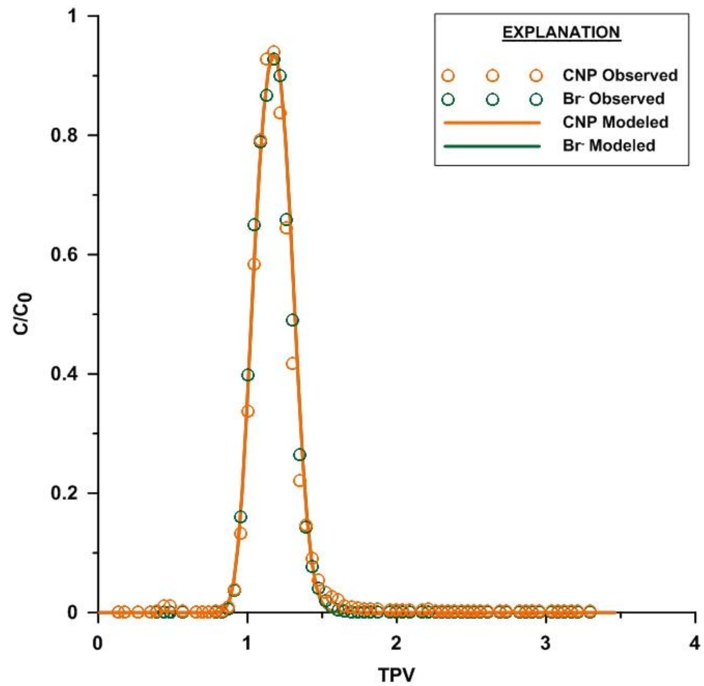
Several 1-dimensional laboratory experiments were performed using columns of porous media of various sizes and reactivity (Figure 1A). These experiments were designed to determine the flow and transport properties of the CNPs under various conditions. For all experiments, a tracer solution containing the CNPs and bromide (Br) was added to the inlet of the column and the concentration versus time was measured at the outlet end (Figure 1B). Bromide was used because in many subsurface environments it acts as a conservative tracer and is widely used in groundwater and column tracer tests. For several of the experiments, the breakthrough curves (BTCs) were analyzed using a 1-D transport model, CXTFIT in order to determine flow and transport parameters for each tracer.

The general designs of the column experiments performed were as follows:

1. Uniform silica sand of 20-30 mesh. These experiments were designed to make sure that the CNPs and Br were transported identically through a homogeneous, non-reactive porous medium. Fitted values of retardation (R, which should be around a value of one) and dispersion coefficient should be identical for both tracers.

2. A heterogeneous column consisting of a small core of coarse sand surrounded by a matrix of finer sand. This experiment was designed to determine if the CNPs are affected by diffusion from the coarse material into the fine material (previous studies suggested that the CNPs did not diffuse as readily as Br). Baffles were placed in the finer material to prevent flow.
3. A similar experiment as above but with flow stopped for 6 days. This interrupt in the flow rate will allow time for both tracers to diffuse into the matrix. If there is diffusion the BTCs should show evidence of this.
4. A final experiment was run using a mixture of the 20-30 mesh silica sand and a surface-modified zeolite. The zeolite should remove Br from the solution but not affect the CNPs.





(A) **(B)**

Figure 1. (A) Illustration of column design. (B) Breakthrough curves of Carbon Nanoparticles and Bromide through the homogeneous column. Note that both tracers are transported nearly identically. The x-axis in time in pore volumes and the y-axis is relative concentration.

Results and Discussion

For Experiment 1, the column used had a 5-cm diameter and was 30 cm in length. CNPs and Br were added as a pulse and the effluent was sampled and the concentrations of CNP and Br were determined. The BTC of the experiment is shown in Figure 1B, with the data as symbols and the model as solid lines. As can be seen, the CNPs and Br were transported through the column identically, with no retardation (R = 1) and with minimal dispersion. This experiment confirmed that CNPS and Br are conservative tracers in this porous medium.

For Experiment 2, the column was designed with a core diameter of coarse sand of 1.3 cm, surrounded by a matrix of fine sand. The BTCs shown in Figure 2 clearly exhibit a significant tailing during the effluent of the tracers, indicating that there is most likely diffusion occurring from the core into the matrix during the influent of the tracer and diffusion from the matrix to the core during the effluent stage. These results are contrary to a previous study which suggested that there was minimal diffusion of CNPs compared to Br during similar tracer experiments.

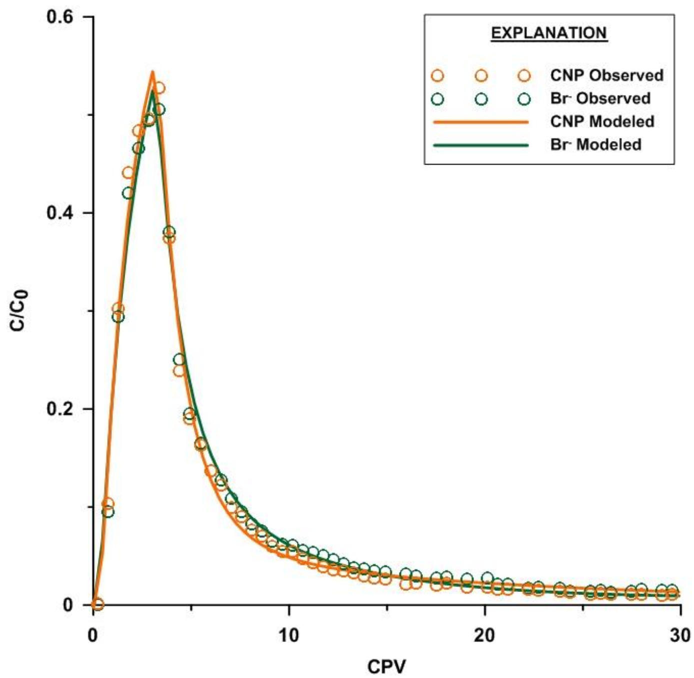
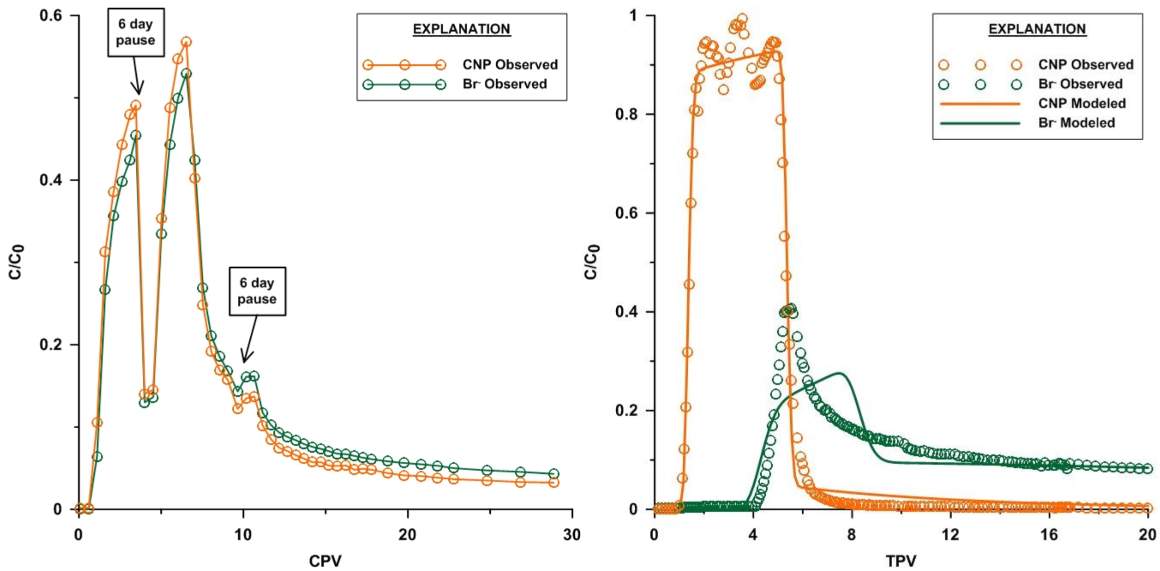


Figure 2. Breakthrough curves of CNPs and Br for the heterogeneous column with a no-flow matrix. Tailing during the elution suggests diffusion from the core into the matrix and back out.

Experiment 3 was designed to emphasize the effects of diffusion. During the stop flow period while the tracer was injected allows significant time for the effects of diffusion to be seen. The BTCs for this experiment (Figure 3A) shows a significant drop in concentration of both tracers following the stop flow period. This is due to the tracers diffusing from the core into the matrix. There was also a stop flow period during the effluent stage and the increase in concentrations seen is due to the tracer diffusing back from the matrix into the core. This confirms the finding of Experiment 2 that the transport of CNPs through a porous medium may be influence by diffusion into immobile pore space in porous media.

Experiment 4 was designed to determine if the transport of the CNPs was affected during flow through a reactive porous medium in which the transport of the dissolved Br is influenced. The BTC (Figure 3B) shows that the transport of the CNPs was minimally affect by the reactive zeolites. The retardation factor was nearly 1 and all the mass injected was recovered. For Br, the breakthrough occurred at a much later time, indicating that it was transported nearly 17 times slower than the CNPs (R = 17). In addition, the mass of Br recovered was much less. Modeling of the Br BTC shows that the assumptions used by CXTFIT were not valid and that additional processes need to be accounted for with future modeling efforts.



(A) **(B)**

Figure 3. (A) Breakthrough curves for CNPs and Br for the heterogeneous core/matrix design. Not the drop in concentration after a six-day stop-flow during injection and the increase of concentration after the six-day stop-flow during elution. Both are evidence of the effects of diffusion on transport. (B) Breakthrough curves of CNPs and Br for the column experiment with a surface modified zeolite as part of the porous medium. Note that there is little or no effect on the transport of CNPS but a significant effect on the transport of Br.

Summary and Implications

The research results presented above are important in understanding the potential of the CNPs to be used as a groundwater tracer. The flow and transport parameters determined from using CNPs as tracers, in both non-reactive and reactive porous media, will be vital in understanding the transport of reactive NPs through the environment. In addition, the CNPs can be used as part of a suite of tracers used together to understand flow and transport of contaminants though porous media, the effectiveness of the delivery of NPs designed for remediation of contaminants, and the development of hydrophobic NPs designed to target a specific contaminant or mineral surface.

Outcomes and Impacts

The funding for this project was used in part to support a graduate student for one semester, Charlene King. The results are being further analyzed by her and will be the basis of a MS thesis.

In addition, Ms. King gave a presentation of the 2015 National Ground Water Association Ground Water Summit in San Antonio, TX. The title of her talk was "Fluorescent

Nanosphere Transport: Groundwater Tracing and Implications for the Migration of Environmental Nanoparticles". Charlene received the Farvolden Award for best student presentation.

Charlene was also awarded a small grant from the Geological Society of America Hydrogeology Division to further support the research beyond what was funded by the Water Center.

Proposals Submitted

The PIs of this projected submitted a proposal to Hydrologic Sciences Division of NSF in December 2014 based on preliminary results of this work: Using "Smart" Nanoparticles to Tracer Groundwater Flow and Characterize Porous Media", requesting $470,013. The proposal was not funded.

A preproposal was submitted to DoD SERDP "Development of Mesoporous Organic-Inorganic Hybrid Nanoparticles to aid in Remediation of perfluoroalkyl compounds in contaminated groundwater", $149,407. The preproposal was not advanced.

The PIs will be working on modifying the NSF proposal to resubmit in 2015.