Stability and Transport of Graphene Oxide Nanoparticles in Groundwater and Surface Water

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Abstract

The effects of groundwater and surface water constituents (i.e., natural organic matter [NOM] and the presence of a complex assortment of ions) on graphene oxide nanoparticles (GONPs) were investigated to provide additional insight into the factors contributing to fate and the mechanisms involved in their transport in soil, groundwater, and surface water environments. The stability and transport of GONPs was investigated using dynamic light scattering, electrokinetic characterization, and packed bed column experiments. Stability results showed that the hydrodynamic diameter of the GONPs at a similar ionic strength (2.1 ± 1.1 mM) was 10 times greater in groundwater environments compared with surface water and NaCl and MgCl₂ suspensions. Transport results confirmed that in groundwater, GONPs are less stable and are more likely to be removed during transport in porous media. In surface water and MgCl₂ and NaCl suspensions, the relative recovery was $94\% \pm 3\%$ indicating that GONPs will be very mobile in surface waters. Additional experiments were carried out in monovalent (KCl) and divalent (CaCl₂) salts across an environmentally relevant concentration range (0.1–10 mg/L) of NOM using Suwannee River humic acid. Overall, the transport and stability of GONPs was increased in the presence of NOM. This study confirms that planar “carbonaceous-oxide” materials follow traditional theory for stability and transport, both due to their response to ionic strength, valence, and NOM presence and is the first to look at GONP transport across a wide range of representative conditions found in surface and groundwater environments.

Key words: artificial groundwater; artificial surface water; graphene oxide nanoparticles; natural organic matter; solution chemistry; stability; Suwannee River humic acid; transport in porous media

Introduction

THE APPLICATION OF ENGINEERED NANOMATERIALS (ENMs) in research, development, and commercial products is widespread and has been growing rapidly (Nel *et al.*, 2013; NRC, 2012). Research into the use of carbon-based nanomaterials [e.g., fullerenes (Guldi *et al.*, 2006), nanotubes (Wang, 2005), and graphene (Brumfiel, 2009, 2012)] has gained significant attention. Specifically, the use of ENMs for consumer electronic device applications (Pumera, 2010) has grown, with major companies investing significant amounts of money into the research and development of graphene (Wang, 2011). In 2010 the production of graphene-based materials was more than 15 tons and that number was predicted to reach >200 tons by 2011 (Wang, 2011). Graphene oxide nanoparticles (GONPs), an oxidized

form of graphene at the nanometer scale (Wang *et al.*, 2011), have also gained a large amount of interest since they exhibit a wide range of mechanical and electronic properties (Duch *et al.*, 2011). For example, GONPs have been proposed to be incorporated into heavy metal detecting sensors (Li *et al.*, 2013b), electrodes (Chen *et al.*, 2012a), and biomedical applications (Li *et al.*, 2013a). However, recent studies have suggested that GONPs can have toxic effects on living organisms (Ahmed and Rodrigues, 2013; Duch *et al.*, 2011). Moreover, increasing studies are reporting bioaccumulation of ENMs in living organisms [e.g., soybean (Priester *et al.*, 2012), tobacco (Judy *et al.*, 2012), and earthworms (Li *et al.*, 2010a)]. In 2006, it was reported that the ingestion of nanoparticles via drinking water or food is possible as a result of accumulation in the environment (Wiesner *et al.*, 2006). To our knowledge, there is no current information regarding the concentration of GONPs present in the environment; however, as the research and development of GONPs increases, portions of these materials will inevitably end up in aqueous environments (Hendren *et al.*, 2013; Lin *et al.*, 2010). A recent study investigating the life cycle analysis for ENMs

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showed that ~80% of carbon nanotubes (CNTs) manufactured will potentially end up in landfills (Keller *et al.*, 2013). It is likely that GONPs will have a similar fate since they have a lot of similarities to CNTs (e.g., nanometer size, carbon-based structure, and application in consumer electronic devices). As a result, transport of GONPs from landfills may cause a potential threat to nearby groundwater or surface water environments. Moreover, there are growing concerns that ENMs such as GONPs will enter natural water bodies at one point in their life cycle (Hammes *et al.*, 2013).

Natural organic matter (NOM) can have a significant effect on the fate and transport of ENMs in groundwater and surface water environments (Akaighe *et al.*, 2013; Furman *et al.*, 2013). Commonly found in natural waters, NOM is a by-product of decaying plant material and is typically present in dissolved form. Typical NOM levels found in most natural waters range from 0.1 to 20 mg/L (Hemond, 2009; Rodrigues *et al.*, 2009). The presence of NOM has been reported to have profound effects on the fate, transport, and even toxicity of ENMs (Aschberger *et al.*, 2011; Pelley and Tufenkji, 2008). Notably, it has been shown that the presence of NOM can reduce the toxic effect of nanoscale zerovalent iron (Li *et al.*, 2010b) and fullerenes (Li *et al.*, 2008). The stability of nanoparticles has also been reported to increase in the presence of humic acid and decrease in the presence of polysaccharides (Espinasse *et al.*, 2007; Wiesner *et al.*, 2008), both of which are forms of NOM. Typically, the humic fraction of the organic material (a high molecular mass compound) makes up the majority of NOM present in most natural waters (Rodrigues *et al.*, 2009; Tchobonaglou and Schroeder, 1987). The presence of humics has been shown to promote the transport of ENMs for metal oxides (e.g., TiO₂; Chen *et al.*, 2012b), silver nanoparticles (Furman *et al.*, 2013), carbonaceous materials [e.g., C₆₀ fullerenes (Chen and Elimelech, 2008) and nanotubes (Chowdhury *et al.*, 2012b)]. Similarly, the transport of 98 nm latex colloids was increased due to the adsorption of humics on the colloids and the silica collectors (Franchi and O'Melia, 2003). Additionally, a recent study demonstrated that the stability of model metal oxide nanomaterials (TiO₂, CeO₂, and ZnO) was reduced due to the adsorption of NOM on the nanoparticles (Keller *et al.*, 2010). For carbon-based materials, humic acid has been reported to greatly increase the stability of fullerene (nC₆₀) nanoparticles as a result of steric hindrance (Qu *et al.*, 2010). In another study, the stability of GONPs was increased in the presence of humic acid at concentrations of 1–10 mg/L Suwannee River humic acid (SRHA) (Chowdhury *et al.*, 2013). A plausible explanation for the increased transport and reduced aggregation is steric stabilization (Elimelech, 1995; Morales *et al.*, 2011), which involves polymers present in humic acid that increase colloidal stability at higher NOM concentrations (e.g., >1 mg/L), which are typically found in surface water environments (Volk, 2001). However, groundwater systems have a much lower concentration (0.1–2 mg/L total organic carbon) (Crittenden 2005). To our knowledge, there are no published articles that investigate the effects of NOM on the transport of GONPs.

In addition to NOM, groundwater and surface water environments also include a complex mixture of ions (e.g., Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, HCO₃⁻, SO₄²⁻) which can have a significant impact on the stability and transport of ENMs (Pensini *et al.*, 2012). Currently there are limited studies that

investigate the effects of complex solution chemistry found in groundwater and surface water environments on the stability and behavior of ENMs (Bennett *et al.*, 2013; Laumann *et al.*, 2013). Moreover, there are only two other studies that have been published that investigate the transport of GONPs specifically in porous media and they were under idealized conditions (e.g., in the presence of a monovalent salt such as KCl or NaCl) (Feriancikova and Xu, 2012).

To address the current limitations in knowledge regarding the stability and transport of GONPs in natural waters and their subsurface environments (e.g., sediment beds); this study systematically investigated complex interactions that are ubiquitous in the environment including the presence of NOM, presence of mono (e.g., K⁺, Na⁺) and divalent ions (e.g., Ca²⁺, Mg²⁺), and co-presence of multiple salts (e.g., MgCl₂ + MgSO₄ + KHCO₃ + NaHCO₃ + CaCO₃) to simulate solution chemistries found in groundwater and surface water environments (Hemond and Fechner-Levy, 2009). An environmentally relevant concentration range of NOM (0.1–10 mg/L SRHA) typically found in groundwater and surface waters (Crittenden, 2012) was chosen to identify the effects of NOM presence on GONP transport in saturated porous media for both monovalent and divalent cations. Artificial groundwater and surface water suspensions were also used to determine the fate and transport of GONPs in each respective aqueous environment. This study was undertaken to bridge the current gap of understanding regarding the fate and transport of GONPs in groundwater and surface water environments by investigating a comprehensive range parameters found in those systems.

Experimental Protocols

Solution chemistry

The detailed procedure used to synthesize the GONPs and the physical dimensions of the materials used in this study have been published previously. The resulting GONPs had a planar structure with an average perimeter of 781 ± 502 nm, an average height of 0.9 ± 0.2 nm, and an average square root of the surface area of 179 ± 112 nm (Chowdhury *et al.*, 2013; Duch *et al.*, 2011). The modified Hummer's method was used to synthesize the GONPs used in this study and were reported to contain oxygen-bearing functional groups including carboxylic, carbonyl, and hydroxyl (Duch *et al.*, 2011).

The GONP suspensions were created at an unadjusted pH since previous studies (Chowdhury *et al.*, 2013; Lanphere *et al.*, 2013) have shown that there is no significant effect on stability from pH 5 to 9. The artificial groundwater (Bolster *et al.*, 1999) and surface water (Yip *et al.*, 2011) suspensions were developed using recipes found in the literature and had an ionic strength (IS) of 3.78 and 1.74 mM, respectively. To compare the effects of solution chemistry at a similar IS (1.5 mM), divalent (MgCl₂) and monovalent (NaCl) salts were used. Additionally, MgCl₂ was investigated across an IS range of 0.3–30 mM to understand its influence on GONP stability and transport.

A concentration of 25 mg/L GONP was used in this study and was prepared by diluting a stock GONP solution into the desired background solution (e.g., CaCl₂) followed by vortexing (Fisher Scientific, Mini Vortexer, Pittsburgh, PA) for 30 s. SRHA was used as the model NOM, and a stock solution of 544 mg/L was prepared using similar methods previously

described in the literature (Chen *et al.*, 2012b; Chen and Elimelech, 2008). Briefly, dry SRHA powder was obtained from the International Humic Substances Society (IHSS, St. Paul, MN) and was dissolved in nanopure ($>18.2\text{ M}\Omega$ at 25°C) deionized (DI) water and stirred for 2 h in the dark. After stirring, the NOM was filtered through a $0.22\text{-}\mu\text{m}$ Millex-GP filter (Millipore Express, Cork, Ireland), pH was adjusted to 5.5 using 0.1 M NaOH , and the resulting solution was stored in the dark at 4°C . For the GONP stability and transport studies, the following conditions were used: a monovalent salt concentration of 31.6 mM KCl in the presence of NOM ($0.1\text{--}10\text{ mg/L}$) and a divalent salt concentration range of $0.1\text{--}10\text{ mM CaCl}_2$ in the absence of NOM and at 1 mM CaCl_2 in the presence of NOM ($0.1\text{--}10\text{ mg/L}$). The KCl and CaCl_2 concentrations in the presence of NOM were chosen since they represent previously reported concentrations at which GONPs are unstable (Chowdhury *et al.*, 2013); therefore, any stabilizing effects in the presence of NOM could be observed. All solutions made in this study were prepared with ACS research grade materials (Fisher Scientific, Pittsburgh, PA) using DI water (nanopure water at $>18.2\text{ M}\Omega\text{ cm}$ at 25°C) and were filtered through a $0.22\text{ }\mu\text{m}$ Millex-GP filter (Millipore Express) prior to use.

Characterization of GONPs

A zetaPALS analyzer (Brookhaven Instruments, Holtsville, NY) was used to determine the electrokinetic properties of the GONPs. Triplicate electrophoretic mobility (EPM) measurements (included five measurements per run) were taken, and the average was determined. Dynamic light scattering (Brookhaven model BI-9000, Holtsville, NY) was used to determine the effective hydrodynamic diameter at a scattering angle of 90° and wavelength of 661 nm . The average hydrodynamic diameter was determined from triplicate runs, which included five measurements per run taken at 2 min per run. Statistical analysis was performed to identify significant differences between data sets by using the Student *t*-test where a 95% confidence level was confirmed when $p < 0.05$.

Transport experiments

An inverted borosilicate glass column (inner diameter of 1.5 cm and a packing depth of 5 cm) was wet packed with high purity quartz sand ($d_{50}=275\text{ }\mu\text{m}$, Iota quartz, Unimin Corp., Spruce Pine, NC) at a porosity of 0.45 ± 0.02 . The quartz sand was cleaned and prepared using previously described methods (Chowdhury *et al.*, 2012a). Peristaltic pumps were used to inject solutions into the column ($1.9 \times 0.1\text{ m/s}$) to simulate the flow of groundwater (Chen *et al.*, 2010; Hemond and Fechner-Levy, 2009). For each experiment the column was packed with new sand and was thoroughly flushed by injecting >10 pore volumes (PVs) of DI water followed by >6 PVs of the background solution of that particular experiment to equilibrate the system (with or without NOM). Next, 6 PVs of the background solution containing GONPs were injected into the column. During transport experiments, the injection solution (containing GONPs and the background electrolyte) was sonicated in a water bath (40 kHz ; Branson 2510) at room temperature ($\sim 25^\circ\text{C}$) prior to injection to prevent aggregation. Additional conservative tracer experiments were conducted using 100 mM KNO_3 to determine an average value of the hydrodynamic dispersion coefficient (D) in the

columns. All transport experiments were conducted in triplicate. Further information regarding the experimental protocol for the transport experiments may be found elsewhere (Lanphere *et al.*, 2013).

To compare the different effects that groundwater, surface water, presence of NOM, and monovalent and divalent salt suspensions had on GONPs during transport, the removal efficiency ($\eta_0\alpha$) and relative recovery (R_r) were calculated from the breakthrough curve (BTC) results. Larger values of the removal efficiency correlate with reduced transport in subsurface environments. The removal efficiency ($\eta_0\alpha$) is an expression that is used to explain the retention of nonspherical particles (e.g., bacteria) (Bolster *et al.*, 2006) in porous media, and it was developed using the combination of the single collector contact efficiency (η_0) and the attachment efficiency (α). The single collector contact efficiency (η_0) is a ratio of the amount of particles that collide with divided by the rate at which particles are headed for the collector (Logan *et al.*, 1995; Rajagopalan and Tien, 1976; Tien *et al.*, 1979). The attachment efficiency (α) is a measure of the successful attachments that collided with the particles (Yao *et al.*, 1971). Together, the removal efficiency ($\eta_0\alpha$) was calculated using the following equation (Bolster *et al.*, 2006; Tufenkji and Elimelech, 2004):

$$\eta_0\alpha = \frac{2d_c}{3(1-\theta)L} \left[\frac{-\ln(R_r) + \ln(R_r)^2}{Pe} \right] \quad (1)$$

The removal efficiency ($\eta_0\alpha$) is a function of the diameter of the collector (d_c , $275\text{ }\mu\text{m}$); length of the packed bed (L , 5 cm); relative recovery (R_r), which is the ratio of the mass of the particles collected divided by the total mass injected; porosity (θ , 0.45); and the Peclet number (Pe , 65), which was determined from the following relationship:

$$Pe = \frac{\nu L}{D} \quad (2)$$

The Peclet number is a function of the interstitial pore velocity (ν), length of the column (L), and the hydrodynamic dispersion coefficient (D). The hydrodynamic dispersion coefficient was determined by fitting the average of triplicate tracer BTCs to the advection-dispersion equation (Fig. 1). The advection-dispersion equation used to model the flow in the column was:

$$\frac{\partial C_T}{\partial t} = \nu \frac{\partial C_T}{\partial x} + D \frac{\partial^2 C_T}{\partial x^2} \quad (3)$$

where C is the reduced concentration (M), t is time (min), x is the pore volume, ν is the interstitial pore velocity (cm/min), and D is the hydrodynamic dispersion coefficient (cm^2/min). The hydrodynamic dispersion coefficient obtained from the model was $0.171\text{ cm}^2/\text{min}$, which correlated with a $Pe=65$ for our packed bed column.

Results and Discussion

Graphene oxide stability

Effect of solution chemistry and NOM. The results from the characterization of the hydrodynamic diameter and electrophoretic mobility for the GONPs as a function of

FIG. 1. Averages of triplicate tracer (100 mM KNO_3) breakthrough curves were fitted from triplicate column experiments using the advection dispersion model. Model efficiency of 0.998 was obtained for the model fits.

CaCl_2 concentration and NOM concentration in the presence of 31.6 mM KCl and 1 mM CaCl_2 are found in Table 1.

In a previous study (Lanphere *et al.*, 2013) the effects of KCl concentration on the stability of GONPs was investigated; however, since the dominant cation present in most aquatic environments is Ca^{2+} , this divalent cation was chosen to simulate more environmentally relevant conditions. In the absence of NOM, the EPM of the GONPs was sensitive to the concentration of CaCl_2 over the range tested (0.1–10 mM), with EPMs varying from -1.7×10^{-8} to $-0.9 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$. In agreement with the EPM data, GONP aggregation was also sensitive to CaCl_2 concentrations as determined by the hydrodynamic diameter of the particles, which increased dramatically from $257 \pm 9 \text{ nm}$ to a particle size greater than the detection limit ($6 \mu\text{m}$) at 0.1 and 10 mM CaCl_2 , respectively. This increase in the hydrodynamic diameter in the presence of Ca^{2+} is more substantial than what has already been reported ($234 \pm 1 \text{ nm}$) for a monovalent salt across a similar salt concentration (1–10 mM KCl; Lanphere *et al.*, 2013). Similar effects have been seen by others (Chowdhury *et al.*, 2013) working with GONPs and were explained using the Schulze-Hardy rule (Overbeek, 1980), which suggests that the coagulating power of the salt as a function of its valence will have dramatic impact on the critical coagulation concentration for particles in solution from reduced electrostatic repulsion forces due to the collapse of the electric double layer.

The effects of NOM on GONP stability were also investigated in the presence of 31.6 mM KCl and 1 mM CaCl_2 as seen in Table 1. Across all NOM concentrations tested (0.1–10 mg/L), the stability of the GONPs was increased and smaller aggregates were observed for both monovalent (K^+) and divalent (Ca^{2+}) cations. The presence of NOM had a relatively minor effect on the EPM of the GONPs in 31.6 mM KCl, and no significant effect ($p > 0.05$) in 1 mM CaCl_2 . Chowdhury *et al.* (2013) observed a similar trend, suggested

TABLE 1. ELECTROKINETIC AND HYDRODYNAMIC DIAMETER PROPERTIES OF GRAPHENE OXIDE NANOPARTICLES IN THE PRESENCE OF NATURAL ORGANIC MATTER AT ELECTROLYTE CONCENTRATIONS OF 31.6 mM KCl AND 1 mM CaCl_2

Solution chemistry conditions	Electrophoretic mobility ($\times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$)	Hydrodynamic diameter (nm)
31.6 mM KCl ^a	-2.7 ± 0.1	1598.1 ± 105.1
0.1 mg/L SRHA	-2.7 ± 0.1	1159.7 ± 63.8^b
1.0 mg/L SRHA	-2.8 ± 0.1	573.7 ± 56.1^b
10 mg/L SRHA	-3.0 ± 0.1	248.8 ± 7.0^b
0.1 mM CaCl_2 ^a	-1.7 ± 0.3	225.1 ± 8.7
1.0 mM CaCl_2 ^a	-1.6 ± 0.1	2797.8 ± 211.6
0.1 mg/L SRHA	-1.6 ± 0.2	2453.5 ± 211.0
1.0 mg/L SRHA	-1.7 ± 0.1	1556.4 ± 182.2^b
10 mg/L SRHA	-1.8 ± 0.1	273.6 ± 7.7^b
10 mM CaCl_2 ^a	-0.9 ± 0.02	ND

Additional stability characterization across a concentration range of 0.1–10 mM CaCl_2 is shown in the absence of natural organic matter (NOM) for comparison.

^aConditions in the absence of NOM.

^bDenotes a statistically significant difference compared to conditions without NOM.

ND, not detectable (diameter observed was greater than $6 \mu\text{m}$ which exceeds dynamic light scattering (DLS) limitations on size characterization); SRHA, Suwannee River humic acid.

that the negligible effect of SRHA on the zeta potential may be due to the sorption of SRHA onto the graphene oxide surface, and claimed that steric repulsion may be the mechanism for this phenomenon. Others have seen similar trends with respect to the effects of IS and NOM on the stability of ENMs (Li *et al.*, 2011b; Saleh *et al.*, 2008). Li *et al.* (2011a) showed that the aggregation rate for CeO_2 was greater at higher KCl and CaCl_2 concentrations, which is similar to the trend we observed in this study for GONP and Ca^{2+} suspensions.

While the presence of NOM did not correlate with any specific trend regarding the EPM of the GONPs, the stability was noticeably altered. In general, for all concentrations of humic acid (0.1–10 mg/L), the GONPs were more stable in the presence of NOM. In KCl, the hydrodynamic diameter was significantly ($p < 0.05$) reduced from $1598 \pm 105 \text{ nm}$ to $1160 \pm 64 \text{ nm}$ with the addition of just 0.1 mg/L NOM. Overall, the diameter in KCl was dramatically reduced $249 \pm 7 \text{ nm}$ at the highest NOM concentration of 10 mg/L. This trend was the same in CaCl_2 suspensions in the presence of NOM where the diameter decreased in size from $2798 \pm 212 \text{ nm}$ to $274 \pm 8 \text{ nm}$ in 0 and 10 mg/L NOM suspensions, respectively. However, for the CaCl_2 suspensions, no significant difference in diameter was observed until an NOM concentration of 1 mg/L NOM was achieved, which is an order of magnitude greater compared with the KCl suspensions in the presence of NOM.

Overall, this trend is consistent with other studies reporting the impact of NOM presence on ENM aggregation. Hyung *et al.* (2006) reported that the stability of carbon nanotubes increased in the presence of Suwannee River NOM (across the range of 10–100 mg/L). Similarly, at the same concentration as used in this study (1 mg/L NOM), Zhang *et al.* (2009) reported

that the propensity of metal oxide nanoparticles (e.g., ZnO, NiO, TiO₂, Fe₂O₃) in 0.01 mM KCl suspensions to aggregate is reduced from the negative charge imparted by the NOM. In the same study, it was reported that the negative charge imposed by NOM to the particle surface was neutralized in the presence of Ca²⁺, which agrees with the current study. This may explain why the EPM of the GONPs was not influenced as a function of NOM in Ca²⁺ suspensions in this study.

Effects of groundwater and surface water environments. The hydrodynamic diameter and EPM of GONPs in surface water and groundwater systems were measured and are shown in Table 2. While the ratios and specific ions present in each respective system are different, the IS was held constant at 2.1 ± 1.1 mM to avoid any potential contributions to stability since GONP sensitivity to IS has been documented (Feriancikova and Xu, 2012; Lanphere *et al.*, 2013). The diameter of the GONPs ranged from 240 to 260 nm across the various types of waters considered in this study except for artificial groundwater (AGW), which had a significantly ($p < 0.05$) higher diameter of 2577 ± 195 nm. The larger diameter associated with the AGW suspensions may be a result of the greater presence of Ca²⁺ ions in that system. It has been reported previously (Chowdhury *et al.*, 2013) that the Ca²⁺ ions can bind with the oxygen functional groups present on the GONPs, which may explain the specific increase in GONP size observed in the AGW compared to the artificial surface water (ASW) suspensions.

The presence of another commonly found divalent cation, Mg²⁺, was examined across an IS range of 0.3–30 mM as seen in Table 2. It was determined that the hydrodynamic diameter of the GONPs remained quite consistent (254 ± 10 nm) at lower IS until 4.5 mM MgCl₂ was achieved when the GONP aggregate reached a diameter of 508 ± 62 nm. At the highest IS tested (30 mM MgCl₂) the GONP diameter was greater than 6 μm (see Table 2), suggesting that any significant sensitivity to IS occurs beyond the typical concentrations (1 mM Mg²⁺) found in aqueous environments (Crittenden, 2005). These re-

sults indicate that the GONPs will be very stable in typical environmental systems and behave similarly in groundwater and surface water environments with comparable Mg²⁺ concentrations.

The EPM of GONPs in aqueous environments was measured, and the results are found in Table 2. The EPM of the GONPs in the AGW was $-1.85 \pm 0.1 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$. Compared with the AGW suspension, the EPM values for the ASW ($-2.19 \pm 0.2 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$) and MgCl₂ ($-1.71 \pm 0.2 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$) at similar IS were not significantly different ($p > 0.05$). In the 1.5 mM NaCl solution, GONPs were significantly ($p < 0.05$) more negatively charged than when suspended in AGW or ASW at a similar IS (3.78 and 1.74 mM, respectively). The higher negative EPM value in the presence of NaCl is in agreement with previously reported trends for GONPs that show the critical coagulation concentration occurs at a much greater IS (44 mM NaCl) than found in ground and surface waters (Chowdhury *et al.*, 2013). When the IS was increased to 10 mM NaCl, a decrease in the magnitude of EPM was observed with a value of $-3.11 \pm 0.4 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$ being recorded, which was significantly ($p < 0.05$) less negative compared with the 1.5 mM NaCl conditions. This decrease in EPM as a function of IS for GONPs in monovalent salts has also been observed in previous studies (Feriancikova and Xu, 2012; Lanphere *et al.*, 2013). For the GONPs suspended in the MgCl₂ solution, EPM values were relatively consistent $-1.72 \pm 0.2 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$ until 30 mM MgCl₂ was achieved. At 30 mM MgCl₂, the EPM was $-1.22 \pm 0.1 \times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$ and was the least stable compared with the lower IS conditions. A similar trend was observed in the other monovalent (NaCl) and divalent (Ca²⁺) systems in which an increase in IS correlated with a decrease in GONP stability as would be predicted by traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Derjaguin and Landau, 1993; Verwey, 1945).

Graphene oxide transport in porous media

Effects of Ca²⁺. Representative BTCs for GONP transport as a function of CaCl₂ concentration are shown in Fig. 2. At the lowest concentration (0.1 mM CaCl₂), ~100% of the GONPs were eluted from the column. As the CaCl₂ concentration increased, a reduction in GONP transport was observed. For example, at 1 mM CaCl₂ an intermediate concentration (compared to the 100% and 0% eluted at the lowest and highest CaCl₂ concentration tested) breakthrough occurred where ~20% of GONPs were eluted from the column. Ripening, a phenomenon by which deposition rates increases with time (Liu *et al.*, 1995), is a potential mechanism for the BTC shape observed at 1 mM CaCl₂. Liu *et al.* (1995) reported a similar trend for colloidal latex particles in the presence of SO₄²⁻ and suggested the BTC shape was a result of the divalent cation adsorbing onto the particle surface resulting in particle destabilization. Moreover, Saleh *et al.* (2008) reported similar BTC shape at the same concentration (1 mM CaCl₂) for surface-modified reactive nano-iron particles and attributed it to the increased particle attachment to sand grains during transport. At the highest concentration (10 mM CaCl₂), only 0.8% of the particles were eluted from column during transport resulting in no specific BTC shape being observed. In another report, the presence of Ca²⁺ was reported to reduce the mobility of

TABLE 2. STABILITY RESULTS FOR GRAPHENE OXIDE NANOPARTICLES AS A FUNCTION OF ARTIFICIAL GROUNDWATER, ARTIFICIAL SURFACE WATER, MgCl₂, AND NaCl

Water type	Ionic strength (mM)	Electrophoretic mobility ($\times 10^{-8} \text{ m}^2/(\text{V} \cdot \text{s})$)	Hydrodynamic diameter (nm)
AGW	3.78	-1.9 ± 0.1	2577.4 ± 195.0
ASW	1.74	-2.2 ± 0.2	240.3 ± 5.8^a
MgCl ₂	0.30	-1.9 ± 0.1	246.6 ± 1.3^a
	1.5	-1.7 ± 0.2	260.9 ± 16.4^a
	3.0	-1.6 ± 0.3	507.0 ± 62.9^a
	30	-1.2 ± 0.1^a	ND
NaCl	1.5	-4.0 ± 0.2^a	233.2 ± 7.1^a
	10	-3.1 ± 0.4^a	261.8 ± 7.5^a

The unadjusted pH of the artificial groundwater (AGW) and artificial surface water (ASW) suspensions were 7.3 ± 0.04 and 8.5 ± 0.9 , respectively. The average ionic strength for all the suspensions was $2.1 \pm 1.1 \text{ mM}$.

^aStatistically significant difference compared to AGW.

FIG. 2. Representative breakthrough curves are shown from triplicate column experiments performed at 25 mg/L GONPs and with varying CaCl_2 concentrations (0.1–10 mM) at room temperature ($\sim 23^\circ\text{C}$). The error bars represent one standard deviation ($n=3$).

aqueous fullerenes ($n\text{-C}_{60}$) and fullerols due to the bridging effect by the Ca^{2+} ions with negatively charged surfaces (Xiao and Wiesner, 2013). This may explain why the transport of GONPs was reduced as a function of CaCl_2 concentration. It is likely that bridging among the Ca^{2+} ions and the oxygen functional groups (e.g., carbonyl and carboxylic) (Duch *et al.*, 2011) on the GONPs was responsible for the decrease in transport as shown by the breakthrough curves in Fig. 2.

Additionally, straining is likely a mechanism that contributed to the transport results in the presence of Ca^{2+} ions. Straining occurs when the ratio of the particles diameter (d_p) and the diameter of the collector (d_c) is greater than or equal to the theoretical threshold of 0.002 (Bradford *et al.* 2002, 2003). At 10 mM CaCl_2 the (d_p/d_g) ratio was >0.02 and correlated with 1% of the GONPs being eluted from the column. This same straining mechanism for GONP removal during transport was observed in a previous study in the presence of ≥ 31.6 mM KCl (Lanphere *et al.*, 2013). Therefore, the intermediate electrolyte concentration (1 mM CaCl_2) was chosen to investigate the presence of NOM on GONP transport since this concentration would allow for the influence of NOM to be clearly seen.

Effects of NOM. The results from the transport study in terms of the removal efficiency and relative recovery are shown in Fig. 3. Overall, the presence of NOM decreased the removal efficiency and increased the relative recovery for both monovalent and divalent cations across the entire range 0.1–10 mg/L NOM tested.

For the 31.6 mM KCl suspensions, a significant difference ($p < 0.05$) was observed in the transport of GONPs after only 0.1 mg/L NOM was added, which is likely attributed to the sorption of NOM onto favorable attachment sites. Overall, the removal efficiency did decrease by 88% and the relative recovery increased by 314% across the range of 0–10 mg/L NOM.

For the CaCl_2 suspensions, no significant difference ($p > 0.05$) in transport was observed following addition of 0.1 mg/L NOM. However, a significant difference ($p < 0.05$) was observed once 1 mg/L NOM was introduced, which is an order of magnitude greater than for the KCl system. Overall, the transport of GONP increased in the presence of NOM and the removal efficiency decreased by 99% across the range 0–10 mg/L NOM. Finally, the relative recovery increased by 565% across the range 0–10 mg/L NOM.

The removal efficiencies and relative recovery values obtained in this study correlate well with the stability characterization results as well as observations of nanoparticle transport reported in the literature in the presence of NOM (Godinez *et al.*, 2013; Wang *et al.*, 2013). In this study, as the concentration of NOM increased, a decrease in removal efficiency and an increase in relative recovery were observed, suggesting that the presence of NOM enhances steric hindrance and subsequently particle stability during transport. This is in agreement with what was observed from the hydrodynamic diameter characterization. However, from 0.1 to 1.0 mg/L NOM, a larger removal recovery was observed in the CaCl_2 compared with the KCl suspension across the same range of organic matter concentration. This difference in removal recovery may be due to a higher degree of adsorption by NOM onto the sand grains in the presence of Ca^{2+} ions. This is similar to a recent transport study in which an increase in deposition of fullerenes onto humic acid and alginate-coated surfaces was attributed to the complex formation of the NOM macromolecules with Ca^{2+} ions, resulting in a reduction in the charge and steric influence of the adsorbed macromolecule layers (Chen and Elimelech, 2008). This mechanism may be responsible for the observed increase in GONPs deposition in CaCl_2 as compared to KCl suspensions at the same NOM concentration. This study is the first to present the coupled factors of NOM and divalent cations that are present in ground and surface waters on the transport of GONPs in porous media under an idealized scenario, selected

FIG. 3. Removal efficiency (A) and relative recovery values (B) obtained from graphene oxide nanoparticles (GONPs) triplicate breakthrough curve data at electrolyte concentrations of 31.6 mM KCl and 1 mM CaCl_2 as a function of NOM concentration.

FIG. 4. Removal efficiency (A) and relative recovery values (B) for GONPs suspended in different water types. GONPs suspensions had the following ionic strengths: AGW (3.78 mM), ASW (1.74 mM), MgCl_2 (1.5 mM), and NaCl (1.5 mM).

to simulate environmentally relevant conditions. Notably, this is the first study to demonstrate the potential for enhanced GONP transport in natural waters in the presence of environmentally relevant NOM concentrations and the presence of K^+ and Ca^{2+} ions, which are ubiquitous in groundwater and surface water environments.

Effects of groundwater and surface water environments. The relative recovery values obtained from the transport studies show the following removal trends $\text{AGW} > \text{ASW} \approx \text{NaCl} \approx \text{MgCl}_2$ (Fig. 4). While the relative recovery was similar ($94\% \pm 3\%$) for the ASW, Mg^{2+} , and Na^+ systems, there was a significantly ($p < 0.05$) lower amount ($54\% \pm 4\%$) of GONPs removed during transport for the AGW suspensions. These results indicate that the majority of GONPs will likely be removed via settling in groundwater systems and be more mobile in the substrate located at the bottom of surface waters (e.g., stream beds, sediment surface).

Additional transport experiments with Mg^{2+} ions were performed as a function of IS to determine at what concentrations GONPs would become less mobile. Across the range of IS tested (0.3–1.5 mM MgCl_2), the average relative recovery was $95\% \pm 1\%$ and there was no significant difference ($p > 0.05$). However, once an IS of 4.5 mM MgCl_2 was achieved, the relative recovery dropped to 12%. This reduction in transport correlates well with the decrease in stability as observed during the sizing analysis described above. Moreover, the removal efficiency was calculated from the relative recovery results to provide insight into GONP transport. The removal efficiency in AGW was ~ 6 times greater than in ASW, confirming the initial assertion that the enhanced amount of divalent ions (e.g., Mg^{2+} and Ca^{2+}) ions in groundwater will play a substantial role in reducing GONP transport in these environments. Additionally, the removal efficiency was 10 and 14 times greater in AGW compared with the Mg^{2+} and Na^+ systems at a similar IS, respectively. Overall, the removal efficiency and relative recovery results suggest that the potential transport of GONPs will be the greatest in surface water stream beds since they have a lower concentration of Ca^{2+} and Mg^{2+} ions present. To help understand these results one may look at straining as a mechanism responsible for removal of GONPs during transport. The diameter range for particles suspended in the ASW, MgCl_2 , and NaCl correlates with a straining factor of 0.001, which is less than the theoretical limit of 0.002 (Bradford *et al.*, 2003, 2005), which suggests that the GONPs will not be

removed via the straining mechanism during transport in porous media under these conditions. However, for the AGW suspensions, a straining factor of 0.01 was observed, which is far greater than the theoretical limit, suggesting that straining may be a mechanism responsible for GONP removal in groundwater environments.

Summary and Conclusions

In the past, limited studies have used simple monovalent salt systems to understand the fate and transport of GONPs in porous media; therefore, more complex systems including the presence of NOM, divalent ions, and a combination of ions present in groundwater and surface water were evaluated in this study. In the presence of NOM for both monovalent and divalent cations, GONPs were shown to become more stable and will therefore have the capacity to travel longer distances in the subsurface and potentially end up disrupting ecosystems or end up in the food chain through bioaccumulation (Li *et al.*, 2010a). The presence of divalent ions (e.g., Ca^{2+} , Mg^{2+}) resulted in GONPs being less stable compared with monovalent ions at similar concentrations in the absence of NOM. The results indicate that there is a significant difference between the behavior of GONPs in groundwater and surface water systems. Since groundwater systems typically have a higher concentration of hardness (e.g., Ca^{2+} , Mg^{2+}) and a lower concentration of NOM, GONPs will tend to become less stable and will eventually settle out or be removed in these subsurface environments. Conversely, for surface waters, where the presence of NOM is greater and the concentration of divalent ions is typically lower, GONPs will remain stable and their transport will be greater in the subsurface layers in natural water bodies. As a result, benthic organisms living on (or in) the sediment surfaces will likely be negatively impacted by the presence of GONPs.

This study has incorporated many levels of complexity to simulate the complex conditions in environmental systems such as groundwater and surface waters and is the first to report their impact on the transport of GONPs in porous media.

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