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Environmental fate of multiwalled carbon nanotubes and graphene oxide across different aquatic ecosystems

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Abstract

The industrial use and widespread application of carbon-based nanomaterials have caused a rapid increase in their production over the last decades. However, toxicity of these materials is not fully known and is still being investigated for potential human and ecological health risks. Detecting carbon-based nanomaterials in the environment using current analytical methods is problematic, making environmental fate and transport modeling a practical way to estimate environmental concentrations and assess potential ecological risks. The Water Quality Analysis Simulation Program 8 (WASP8) is a dynamic, spatially resolved fate and transport model for simulating exposure concentrations in surface waters and sediments. Recently, WASP has been updated to incorporate processes for simulating the fate and transport of nanomaterials including heteroaggregation and phototransformation. This study examines the fate and transport of multiwalled carbon nanotubes (MWCNT), graphene oxide (GO) and reduced graphene oxide (rGO) in four aquatic ecosystems in the southeastern United States. Sites include a seepage lake, a coastal plains river, a piedmont river and an unstratified, wetland lake. A hypothetical 50-year release is simulated for each site-nanomaterial pair to analyze nanomaterial distribution between the water column and sediments. For all nanomaterials, 99% of the mass loaded moves through systems of high and low residence times without being heteroaggregated and deposited in the sediments. However, significant accumulation in the sediments does occur over longer periods of time. Results show that GO and rGO had the highest mass fraction in the water column of all four sites. MWCNT were found predominantly in the sediments of the piedmont river and seepage lake but were almost entirely contained in the water column of the coastal plains river and wetland lake. Simulated recovery periods following the release estimate 37+years for lakes and 1–4years

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Appendix A. Supporting Information (SI)

for rivers to reduce sediment nanomaterial concentrations by 50% suggesting that carbon-based nanomaterials have the potential for long-term ecological effects.

Keywords

Nanomaterials; WASP; Fate and transport; Multiwalled carbon nanotubes; Graphene oxide

1. Introduction

The broad industrial applications of carbon-based engineered nanomaterials have caused a rapid increase in their production over the last few decades (Novoselov et al., 2012; Stark et al., 2015; Zhu et al., 2010). Graphene oxide (GO) and reduced graphene oxide (rGO) have a wide range of applications in electronics, energy storage, biomedical industries, and optics (Y.G. Sun et al., 2017; Wang et al., 2017; Wei et al., 2017; Wu et al., 2012). Multiwalled carbon nanotubes (MWCNT) are used in polymer composites to increase tensile strength and electrical conductivity (Chinnappan et al., 2018; Jafari et al., 2017; Li et al., 2017). De Volder et al. (2013) report a global carbon nanotube production capacity exceeding several thousand tons per year. An estimated 700 tons of graphene are produced per year in the US and China alone (Ren and Cheng, 2014). Limited only by the cost efficiency of mass production, these numbers are expected to increase as new technologies emerge.

Though there are currently many gaps in knowledge on the potential life cycle pathways of carbon-based nanomaterials, studies show that as they reach product end-of-life some will inevitably be introduced to the aquatic environment (Keller and Lazareva, 2014; Park et al., 2017; Suarez-Iglesias et al., 2017); however, many of these materials have not been systematically investigated for potential human and ecological health risks.

Cytotoxicity towards bacteria, algae, and animal cells has been observed for GO and rGO (Du et al., 2016; Liu et al., 2011; Wojtoniszak et al., 2012; Zhao et al., 2014). Other studies report ecotoxicity and potential for trophic transfer and bioaccumulation of MWCNT (Chen et al., 2012; Mortimer et al., 2016; Shrestha et al., 2013). Further, environmental processes such as transformation and degradation can alter the original state of these materials, affecting their fate, transport, and toxicity (Zhao et al., 2014). Sunlight exposure has been shown to transform and destabilize GO, partially converting it to rGO, CO₂, and polycyclic aromatic hydrocarbons (PAHs) (Hou et al., 2015). A recent study by Adeleye et al. (2018) also observed oxidative degradation of Bisphenol A (BPA) caused by GO and rGO in the presence of sunlight over a 48-hour period. It is therefore crucial to understand the distribution of these nanomaterials in the water and sediments to estimate potential environmental concentrations.

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been widely used to describe the behavior of nanomaterials in the aquatic environment (Praetorius et al., 2014).

Nanoparticle surfaces are modified by the adsorption of natural organic matter suspended in natural waters, a function of the dissolved organic carbon (DOC), pH, and ionic strength of the water, which stabilizes them and allows them to be dispersed in suspension (Chang and Bouchard, 2016; Gigault et al., 2012; Liu et al., 2012). Heteroaggregation of nanoparticles

with suspended particulate matter (SPM) is a site-specific parameter related to suspended nanoparticle stability and SPM concentrations. Homoaggregation, or nanoparticle self-attachment, is less significant for nanomaterials in the aquatic environment because of their stability in natural waters and their small concentration relative to natural suspended sediment concentrations (Bouchard et al., 2015; Keller and Lazareva, 2014; Praetorius et al., 2012; Quik et al., 2014). Under this assumption, the most relevant processes determining the fate and transport of carbon-based nanomaterials are heteroaggregation and phototransformation.

Current analytical methods for detecting and quantifying carbon-based nanomaterials in environmental matrices are difficult to implement due to the problem of distinguishing between natural and engineered concentrations (Gottschalk et al., 2013; Montano et al., 2014; Nowack et al., 2015). Potential environmental concentration estimates using material flow analysis (MFA) and life cycle assessments (LCA) can provide valuable initial estimates, but more detailed models are needed to capture the spatial variability and governing processes of nanomaterials in the aquatic environment (Baalousha et al., 2016; Garner et al., 2017; Gottschalk et al., 2011; Liu and Cohen, 2014). In the absence of measured concentrations, environmental fate and transport models can provide spatially and temporally explicit estimates of environmental concentrations to assess potential ecological exposures (Dale et al., 2015; Praetorius et al., 2012; Quik et al., 2015). Further, recent studies have explicitly modeled the fate and transport of nanomaterials using site-specific heteroaggregation and phototransformation rates (Bouchard et al., 2017; Han et al., in press). However, no studies to date have investigated how these materials behave across different aquatic ecosystems.

The Water Quality Analysis Simulation Program (WASP) is a dynamic, spatially resolved differential mass balance fate and transport model that has been widely used globally for simulating the fate and transport of contaminants in surface waters (Boutilier et al., 2011; Caruso et al., 2008; Yao et al., 2015). The most recent version, WASP8 (WASP, version 8), incorporates processes for simulating the fate and transport of nanomaterials, including heteroaggregation and phototransformation (Ambrose et al., 2017; Knightes et al., in press). Watershed and hydrodynamic models can be linked to WASP8 to provide spatiotemporally explicit inputs for large-scale watershed modeling.

In this study, we investigate the behavior of MWCNT, GO and rGO in the water column and sediments at four different locations. We simulate the loading of nanomaterials over time to understand (1) exposure concentrations in the water column and sediments and how different water chemistry and surface water types affect the development of concentrations over time, (2) spatial distribution across media over time, and (3) how systems respond after the source is removed. Sediment heteroaggregation attachment efficiency (α) values were measured for each nanomaterial at four sites in the southeastern United States including a seepage lake (Lake Barco, FL), a coastal plains river (Brier Creek, GA), a piedmont river (Yadkin River, NC), and an unstratified, wetland lake (Lake Waccamaw, NC). In the absence of adequate analytical methods for detecting carbon-based nanomaterials in the field, this research aims to gain a better understanding of the distribution and potential exposure concentrations of

MWCNT and GO-rGO in surface waters which can then be used to evaluate ecological and human exposure risks.

2. Materials and methods

2.1. WASP model structure

All four sites were modeled with a water column, surface sediment, and subsurface sediment layer for each model segment. Solids were grouped into four state variables (sand, silt, clay, and particulate organic matter) parameterized by density, particle diameter, and settling and resuspension rates. Silt, clay, and particulate organic matter (POM) are input into the water column as concentrations and available for heteroaggregation, whereas sand is contained only in the sediments due to high settling rates. Average flows, suspended solids, and DOC are simulated, with constant inflows and concentrations in each segment. A spin-up period was simulated in each system to allow solid concentrations to reach steady state in the water column and sediments (See SI). WASP simulates the following kinetic processes: heteroaggregation of nanoparticles to suspended particles, attenuation of light from the surface through the water column, and phototransformation of GO to rGO. Details of these processes are described below.

2.1.1. Heteroaggregation—Attachment of nanoparticles to suspended solids is modeled using heteroaggregation kinetics based on colloidal theory and as presented by Praetorius et al. (2012):

$$k_{het} = \alpha k_{coll} N_{SPM} \quad (1)$$

where k_{het} is the heteroaggregation rate constant (#/d), α is the attachment efficiency (unitless); k_{coll} is the rate of collision between nanoparticle and SPM (m^3/d); and N_{SPM} is the number of natural suspended particles per volume ($\#/m^3$). k_{coll} is defined by the equation:

$$k_{coll} = \frac{2k_B T_w (r_N + r_{SPM})^2}{3\mu_w r_N r_{SPM}} + \frac{4}{3} G (r_N + r_{SPM})^3 + \pi (r_N + r_{SPM})^2 |v_N^s - v_{SPM}^s| \quad (2)$$

where k_B is the Boltzmann constant ($1.38 \times 10^{-20} \frac{m^2 g}{s^2 K}$); T_w , G , and μ_w are the absolute temperature (K); shear rate ($1/s$); and dynamic viscosity of water ($\frac{g}{m s}$); r_N and r_{SPM} represent the radii of nanoparticle (nm) and SPM (mm); and v_N^s and v_{SPM}^s are the nanoparticle and SPM settling velocities (m/d). N_{SPM} is expressed by the equation:

$$N_{SPM} = \frac{[SPM]}{\frac{4}{3} \pi \rho_{SPM} r_{SPM}^3} \quad (3)$$

where $[SPM]$ and ρ_{SPM} are the concentration (mg/L) and density of SPM (g/cm³).

While, $[SPM]$ is input and output in mass concentration, WASP internally converts $[SPM]$ into number of particles for these calculations, using particle diameters, settling rates, and characteristics of the system. Because α is a site-specific parameter, it must be estimated or measured experimentally.

2.1.2. Light Attenuation—Phototransformation of nanomaterials in surface waters depends on the light intensity in the water column. The amount of solar radiation that reaches surface waters depends on the time of day and varies throughout the year. Cloud cover and shading attenuate light in the atmosphere. Using a time series of total solar radiation data at the water surface, WASP8 groups the electromagnetic spectrum into 11 bands, (Table SI 4) with five UV bands, five photosynthetically active radiation (PAR) bands, and one infrared band. The fraction of each band varies based on latitude, with increasing UV approaching the equator. As light at the water surface travels through the water column, it is further attenuated by wavelength with depth following the Beer-Lambert law:

$$I_{z,\lambda} = I_0 k_{band,\lambda} e^{-K_{e,\lambda} z} \quad (4)$$

where for each wavelength band λ , $I_{z,\lambda}$ is the light intensity (W/m²) at depth z ; I_0 is the light intensity (W/m²) at the water surface; $k_{band,\lambda}$ is the fraction of light intensity (latitude specific); and $K_{e,\lambda}$ is the light extinction coefficient (1/m) at a specific depth z below the water surface (m). The light extinction coefficient consists of factors that contribute to light attenuation within the water column including the water medium itself, and concentrations of suspended DOC and solids. For each wavelength band, WASP8 calculates the attenuation through the water column using the equation:

$$K_{e,\lambda} = K_{w,\lambda} + K_{DOC,\lambda}[DOC] + K_{TSS,\lambda}[TSS] \quad (5)$$

where for a specific wavelength band λ , $K_{w,\lambda}$ (1/m) is the light attenuation coefficient of water; $K_{DOC,\lambda}$ (1/m) is the light attenuation coefficient due to *DOC*; and $K_{TSS,\lambda}$ (1/m) is the light attenuation coefficient due to suspended solids. $[DOC]$ is the total dissolved organic carbon concentration (mg/L) and $[TSS]$ is the total suspended solids concentration (mg/L).

For each water column layer within a segment, the average light intensity of each wavelength band is given by:

$$I_{av,\lambda} = \frac{1}{z} \frac{I_0 k_{band,\lambda} - I_{z,\lambda}}{K_{e,\lambda}} \quad (6)$$

which can then be summed to get total average light intensity.

2.1.3. Photochemical reactions—Once light attenuation in the water column has been accounted for, the average light intensity in each wavelength band can be used to calculate the phototransformation of GO to rGO. Previous work determined the phototransformation reaction yield of GO to rGO to be 0.55 g-Carbon rGO/g-Carbon GO using the change in measured carbon concentrations from simulated sunlight exposure over time (Hou et al. 2015). The phototransformation of GO to rGO can be described by the first order kinetic equations:

$$\frac{d[GO]}{dt} = -k_{photo}[GO] \quad (7)$$

$$\frac{d[rGO]}{dt} = -Yk_{photo}[GO] \quad (8)$$

Where [GO] and [rGO] are the graphene oxide and reduced graphene oxide concentrations (ng/L); k_{photo} is the overall phototransformation rate constant (1/d); and Y is the phototransformation reaction yield (g-Carbon rGO/g-Carbon GO). k_{photo} is the sum of the wavelength specific product of reaction rate constant and average light intensity for each specific wavelength at a given location, using the equation:

$$k_{photo} = \sum_{i=1}^{10} k_{\lambda,i} I_{avg,\lambda} \quad (9)$$

Details on the calculation of GO wavelength-dependent phototransformation reaction rates are provided in the SI.

2.2 Study sites

Four sites within the southeastern United States with varying hydrology and physical and chemical characteristics (Fig. 1) were studied. Ecosystems included a coastal plains river in Georgia, a small seepage pond in Florida, and a piedmont river and bay lake in North Carolina. Physical characteristics are summarized for each site in Table 2. Whereas average observed DOC concentrations are similar between sites (6 ± 0.8 mg/L), average observed TSS concentrations vary between 2.5 mg/L in Lake Barco to 28 mg/L in the Yadkin River. Average water column depths range from 2.3 to 4.5 m.

2.2.1. Watersheds—Brier Creek is a tributary of the Savannah River, located in coastal Georgia. The Brier Creek watershed consists primarily of forest (39%), wetlands (16%), agricultural-cropland (14%) and grassland (11%) with some urban (7%), agricultural-pasture (7%) and upland shrub land (6%). The Brier Creek WASP model, which is adapted from Bouchard et al. (2017), consists of 12 segments longitudinally with two tributary segments. The total river distance from headwaters to the outflow gage (United States Geological Survey (USGS) streamgage 02198000) is approximately 82 miles, with an average residence time of 2.4 days and an average residence time of 0.20 days per segment. Average suspended

solid concentrations and sediment concentrations were obtained from USGS gage 02197830. Tables SI 7–10 contain model inputs for Brier Creek.

Yadkin River is a part of the Yadkin-Pee Dee River Basin located in northern North Carolina. It is one of the largest rivers in NC and eventually becomes the Pee Dee River at the confluence of the Uwharrie River. Major land uses in the Yadkin River watershed include forest (52%), agriculture-pasture (24%) and urban (16%) with some grassland (4%), upland shrub land (3%) and wetlands (1%). The Yadkin River WASP model domain consists of nine segments between USGS gage 02112000 just below the Wilkesboro Dam to USGS gage 02116500 at Yadkin College (Fig. 1). Total modeled river distance is approximately 92 miles with a residence time of about 3.1 days and an average residence time of 0.34 days per segment. Suspended sediment data from five USGS gages (Fig. SI 2) were used to parameterize the WASP model. Bed sediment samples were collected at segments one, three, seven, and nine and analyzed by the University of Georgia Laboratory for Environmental Analysis for particle size fraction analysis and TOC measurements (Fig. SI 2). Tables SI 13–18 contain model inputs for Yadkin River.

Hydrological Simulation Program – Fortran (WinHSPF 3.0) was used to model streamflow inputs for segments in both Brier Creek and the Yadkin River. HSPF models were calibrated to the observed outflow gage using PEST (Doherty 2001) and the mean annual discharge at each segment was used in WASP. WASP was configured to use the kinematic wave transport mode to route flow through water column segments, which require segment volume dimensions, minimum depth, bottom slope, manning roughness coefficient, and channel geometry coefficients. Tables SI 7 and SI 13 show the hydraulic input parameters for Brier Creek and the Yadkin River.

2.2.2. Water bodies—Lake Barco is a small seepage lake in northern Florida with negligible flow contributions from the surrounding watershed. The lake receives groundwater flow from the north side of the lake and the flow seeps through the southern end but there is no advective loss of particulates in the water column (Pollman et al. 1991). Lake Barco has an average depth of four meters and an area of 0.12 km² (Katz et al. 1995). The sediments in Lake Barco are predominantly fine sands with some clay and silt sized particles (Katz et al. 1995, Readle 1990). The WASP model for Lake Barco, consisting of a single segment, is based on a previous model used in Knightes et al. (2009). Sacks et al. (1992) reports a burial rate of around 0.1 cm/yr. Tables SI 19–21 contain inputs for the Lake Barco WASP model.

Lake Waccamaw is the largest of the natural bay lakes on the North Carolina coastal plain. The surrounding watershed is flat with ubiquitous wetlands and waterways (Knightes et al. 2009). Lake Waccamaw has a surface area of 36 km² with an average depth of 2.3 m (Casterlin et al. 1984). Big Creek is the main source of inflow, draining into Lake Waccamaw from the north with a mean flow rate of 2.0 m³/s. Total inflow to Lake Waccamaw is 2.6 m³/s. The upper Waccamaw River drains out of the lake on the south side from a weir dam. In a report by Riggs et al. (2000), solids suspended in the water column consist of fine organic matter and small amounts of clay. Sediments in Lake Waccamaw consist of a broad, flat bottom of gyttja (mud) and peat encircled by sandy shallows (Frey

1949). Stager and Cahoon (1987) estimate the burial rate in Lake Waccamaw to be around 0.075 mm/yr. The Lake Waccamaw model domain is a single segment with a residence time of 370 days. Tables SI 22–25 contain inputs for the Lake Waccamaw WASP model.

2.3 WASP nanomaterial parameterization

Fig. 2 shows the conceptual model of MWCNT and GO-rGO in a WASP segment for the four systems. As per DLVO theory, heteroaggregation is assumed to be an irreversible process under constant background water chemistry conditions. Additionally, for GO-rGO simulations, once GO heteroaggregates to a solid particle it no longer phototransforms to rGO (i.e., a GO particle heteroaggregated with a solid will not produce an rGO-solid). All scenarios in this study are modeled as a hypothetical release in wastewater treatment plant effluent. A continuous 0.1 kg/d nanomaterial load is simulated in the headwaters (for rivers) based on estimates from previous studies (Sun et al. 2017a). At each site, MWCNT and GO-rGO releases are simulated with a constant load for 50-years (loading period), followed by no load for 100 years (recovery period).

Water column samples were collected at each site and analyzed for DOC, naturally occurring ions, particulate organic matter (POM) and SPM concentrations (Tables SI 1 and SI 2). The α 's for MWCNTs, GO, and rGO were measured in the laboratory for each system using methods described in Bouchard et al. (2017) and Han et al. (2018, In Review). Nanomaterial diameters and α 's were used to parameterize site-specific WASP models. Hourly solar radiation data from the North American Land Data Assimilation System (NLDAS) were collected using methods described in the SI using the waterbody centroid as the input coordinates for each site. NLDAS data (<https://ldas.gsfc.nasa.gov/nldas>) was downloaded from January 1, 1995 to January 1, 2015 (EST) (20 years) and replicated to generate a 50-year time series (Mitchell et al. 2004).

2.3 Calculation of mass fraction

The fraction of nanomaterial mass refers to the proportion of mass of all phases (free and heteroaggregated) in a specific layer (water column, surface sediments, or deep sediments) of an individual segment relative to the total nanomaterial mass of that segment at a given site. MWCNT mass fraction is calculated using the equation:

$$f_{MWCNT,i,l} = \frac{[MWCNT]_{i,l}V_{i,l}}{\sum_{l=1}^L [MWCNT]_{i,l}V_{i,l}} \quad (10)$$

where $[MWCNT]_{i,l}$ is the total concentration of MWCNT in segment i and layer l , and $V_{i,l}$ is the volume of layer l in segment i . GO and rGO mass fractions are calculated relative to the total mass of both GO and rGO.

$$f_{GO,i,l} = \frac{[GO]_{i,l}V_{i,l}}{\sum_{l=1}^L [GO]_{i,l}V_{i,l} + [rGO]_{i,l}V_{i,l}} \quad (11)$$

$$f_{rGO,i,l} = \frac{[rGO]_{i,l} V_{i,l}}{\sum_{l=1}^l [GO]_{i,l} V_{i,l} + [rGO]_{i,l} V_{i,l}} \quad (12)$$

Fig. 4 shows the mass distribution of MWCNT, GO and rGO at all sites during the loading period. Midstream segments are used for Yadkin River and Brier Creek. Similar results for upstream and downstream segments of Yadkin River and Brier Creek are plotted in Fig. SI 6–7.

3. Results and discussion

3.1. Measured attachment efficiencies (α)

Table 2 shows the particle diameters and α values of MWCNT, GO, and rGO in each of the four ecosystems as measured in the laboratory. No significant homoaggregation was measured in any of the site-nanomaterial combinations, indicating that measured nanomaterial removal from the water phase was due to heteroaggregation. MWCNT were not suspendable in Lake Barco and Yadkin River samples. For Lake Barco and Yadkin River simulations, MWCNT were modeled as solid particles that do not attach to other solids in the water column or sediments. MWCNT particles in these two systems moved by advection, settling, and resuspension. The α values were measured for GO and rGO at all four sites. There was no significant GO heteroaggregation for Brier Creek; i.e., there was no removal of GO from the water phase due to attachment on Brier Creek SPM. Therefore, in Brier Creek simulations, GO loaded into the system that did not phototransform into rGO was transported solely by advection from upstream to downstream segments.

Measured α values ranged from 9.9×10^{-8} to 1.7×10^{-5} (unitless) between all sites and nanomaterials. GO in Lake Waccamaw exhibited the highest observed α value (1.7×10^{-5}) of all nanomaterials measured, while GO in Lake Barco was the lowest (1.0×10^{-7}). The highest and lowest α 's for rGO were in the Yadkin River (1.4×10^{-5}) and Brier Creek (3.0×10^{-7}). It is difficult to make generalizations about the relationship between site properties, nanomaterial stability in the water column, and attachment efficiency values since α is dependent on the ionic strength, DOC concentrations of the water, and the mineralogical composition (rarely known) of the sediments. DOC has been shown to play a critical role in stabilizing carbon-based nanomaterials in water and therefore on attachment efficiency values (Chang et al., 2015; Hyung et al., 2007). The observation that MWCNT were not suspendable in Lake Barco and Yadkin River water samples was due to their low total organic carbon concentrations (1.6 and 3.3 mg/L). Additionally, the Yadkin River also had a high cationic strength (Brier Creek $\approx$ Yadkin $>$ Waccamaw $>$ Barco), which would also have impeded MWCNT dispersion and stability in the water column.

In the case of metal nanomaterials, where particles exhibit a positive charge, α can usually be assumed to be one (Dale et al., 2015). Consequently, contact between a metal nanoparticle and suspended solids always result in heteroaggregation, leading to faster removal from suspension by settling. However, the same assumption cannot be made for carbon-based nanoparticles which have an overall negative charge when suspended in

natural waters. For these nanomaterials, α values range temporally and spatially for each specific location as a function of pH, ionic strength, and DOC concentrations. The results from this study show that the range of measured α values for all nanomaterial-site pairs are outside the sensitive domain of this parameter (<0.01) (Bouchard et al., 2017; Praetorius et al., 2012) by several orders of magnitude, suggesting that estimations of α for carbon-based nanomaterials may be reasonable in the absence of laboratory measurements. Further research is needed to determine if this is widely spatially and temporally applicable. However, it should also be considered that even small α values can lead to accumulation in the sediments over long time periods due to irreversible heteroaggregation.

3.2. Accumulation during loading period

Simulated nanomaterial concentrations over the 50-year loading period are shown at each site in Fig. 3. Midstream segments are shown for river sites. In the water column, concentrations decrease in river segments moving away from the source. Sediments in the Yadkin River follow this trend, whereas in Brier Creek the opposite is observed (Figs. SI 4–5). Freely suspended nanomaterials make up 99.9% of the concentration in the water column at all sites during this period. Sediment concentrations refer to total nanomaterial concentrations in the sediment layers.

3.2.1. MWCNT—During the 50-year loading period, MWCNT concentrations reached steady state in the water column at all sites except Lake Barco. Steady state concentrations in the water column were reached within two years in Yadkin River and Brier Creek and about 10 years in Lake Waccamaw. Only the river systems achieved steady state in the surface sediments within the loading period, with segments in Yadkin River ranging from 2 to 3 years and Brier Creek ranging from 20 to 44 years. No site reached steady state in the deep sediments within the loading period. Maximum concentrations in the water column, surface sediments and deep sediments of each nanomaterial-site pair are shown in Table 3. After 50 years, Lake Barco had the highest MWCNT concentrations overall, accumulating 5.0×10^3 ng/L in the water column and 9.7×10^8 and 9.6×10^7 ng/kg in the surface sediments and deep sediments respectively. These concentrations were much higher than all other sites, which is due to the lack of outflow in Lake Barco. Yadkin River accumulated the lowest MWCNT concentration in the water column (2.4 ng/L) while Brier Creek MWCNT concentrations were lowest in the surface sediments (4.9 ng/kg) and deep sediments (2.9 ng/kg).

3.2.2. GO-rGO—Due to the varying intensity of solar radiation throughout the day and seasonally, GO and rGO concentrations oscillate over time and never reach a constant value. Therefore, comparisons between sites for GO and rGO are based on average concentrations in the last year of the loading period (year 50). Lake Barco accumulated the highest average rGO concentrations in all layers and average GO concentrations for all layers except surface sediments, due to the slow removal of sediments. Average concentrations of GO in Lake Barco were 8.3×10^3 ng/L ($\pm 3 \times 10^3$ ng/L) in the water column, and 2.1×10^2 ng/kg (± 4 ng/kg) in the deep sediment layer, while rGO concentrations were 2.1×10^6 ng/L ($\pm 22 \times 10^4$ ng/L) in the water column and 1.3×10^6 ng ($\pm 3 \times 10^4$ ng/kg) and 7.9×10^4 ng/kg ($\pm 3 \times 10^3$ ng/kg) in the surface sediments and deep sediments. Lake Waccamaw had the highest average concentration of

GO in the surface sediments layer, reaching $1.6 \times 10^4 \text{ ng/kg}$ ($\pm 2 \times 10^2 \text{ ng/kg}$). The Yadkin River had the lowest average concentrations of GO in the water column ($23 \pm 1 \text{ ng/L}$), surface sediments ($5.2 \pm 6 \times 10^{-3} \text{ ng/kg}$), and deep sediments ($1.1 \pm 1 \times 10^{-2} \text{ ng/kg}$). Lowest average rGO concentrations in the water column were observed in Yadkin River ($1.2 \times 10^{-1} \pm 1 \times 10^{-1} \text{ ng/L}$), while in the sediment layers, Brier Creek concentrations were the lowest ($4.1 \times 10^{-3} \pm 6 \times 10^{-5} \text{ ng/kg}$ in surface sediments and $2.5 \times 10^{-3} \pm 2 \times 10^{-5} \text{ ng/kg}$ in deep sediments). Overall river sites had higher GO concentrations than rGO whereas rGO concentrations exceeded GO concentrations in the two lakes.

3.2.3. Overall trends—For all sites, visible light makes up at least 98% of total average light intensity in the water column, with ultraviolet contributions between 1 and 2% (Fig. SI 1). Hou et al. (2015) showed that although ultraviolet light makes up a small portion of total light intensity, it is the most significant contributor (99%) in GO phototransformation. At all four sites, TSS is the largest contributor to overall average light attenuation in the water column whereas DOC is the largest contributor to light attenuation in the ultraviolet wavelengths.

Patterns emerge when comparing the accumulated concentrations of nanomaterials between sites in each segment layer (water column, surface sediments, and deep sediments). In the water column, MWCNT and GO concentrations are similar between river sites. rGO concentrations show a distinct difference between site type in all layers, with rivers accumulating lower concentrations compared to GO while lake concentrations exceed GO. Lake Waccamaw, which is the only site to have heteroaggregation for all nanomaterials, shows similar nanomaterial concentrations within each layer.

3.3. Mass fractions of MWCNT, GO and rGO

Fig. 4 shows the mass distribution of MWCNT, GO and rGO at all sites during the loading period. Midstream segments are used for Yadkin River and Brier Creek. Similar results for upstream and downstream segments of Yadkin River and Brier Creek are plotted in Figs. SI 6–7.

3.3.1. MWCNT—During the loading period, MWCNT mass in Lake Waccamaw was primarily in the water column with a slow transfer of mass to the surface sediments due to net deposition. After 50 years of constant loading, 92% of MWCNT mass remained in the water column while approximately 8% by mass accumulated in the surface sediments. Brier Creek, with a much shorter residence time, did not accumulate much mass in the sediments during the loading period. In fact, 99.9% of MWCNT mass in Brier Creek was contained in the water column throughout this period. In the case of Lake Barco and Yadkin River, MWCNT were modeled as solid particles with no attachment to solids in the water column or sediments. Due to the large particle diameter (D_h) of MWCNT at these sites, particles settled quickly, accumulating in the sediments. After the initial spike in mass in the surface sediments, MWCNT mass slowly shifted into the deep sediments via burial. At the end of the loading period, 66% of MWCNT mass in Lake Barco accumulated in the surface sediments with about 34% in the deep sediments. The Yadkin River accumulated 56% of MWCNT mass in the surface sediments and 34% in the deep sediments. MWCNT mass in

the sediments increased slightly in Brier Creek segments moving away from the source. In the Yadkin River, the water column and surface sediments saw an increase in MWCNT mass moving downstream from the source.

3.3.2. GO-rGO—Fig. 4, displays a clear pattern in the mass transfer from GO to rGO for systems with different residence times. For the two lakes, total mass quickly shifts from 100% GO to mostly rGO in the water column. However, in the two river systems, only a small fraction of GO is converted to rGO over the course of the loading period. The increased exposure of GO to solar radiation in systems with longer residence times allows for more phototransformation to rGO. At the end of the loading period, rGO makes up 99% of total mass in Lake Barco and 73% of the total mass in Lake Waccamaw. The rGO mass in Yadkin River and Brier Creek is <1% of the total nanomaterial mass in the system. Looking at the mass fractions of GO and rGO relative to themselves (e.g., rGO in water column vs total rGO in segment), we can see that for all sites except Lake Waccamaw, 99%+ of GO and rGO accumulated in the water column at the end of the loading period. GO in Brier Creek did not heteroaggregate, so all mass was contained in the water column. Lake Waccamaw contained a higher percentage of rGO and GO mass in the surface (19–26%) and deep sediments (2–3%). Yadkin River saw a slight increase in GO and rGO mass fractions in the sediment layers moving downstream, whereas Brier Creek mass distributions remained consistent across segments.

3.3.3. Overall trends—Because some nanomaterials did not reach steady state in the surface and deep sediment layers during the 50-year loading period, the fractions of mass in each compartment are still adjusting. From Fig. 4 we can see that the mass fractions are still rising in the sediment layers of Lake Barco (GO and rGO mass sediment fractions are rising, just very slowly), Lake Waccamaw, and in the case of MWCNT, Yadkin River. If the loading period were extended beyond the 50-year simulation, nanomaterial mass in the sediments would eventually exceed nanomaterial mass in the water columns of Lake Waccamaw and Lake Barco. Yadkin River and Brier Creek sediment fractions would increase some in the deep sediments, but the overall mass distribution would not change much from the 50-year simulation.

3.4. System response during recovery period

A recovery period is simulated for each nanomaterial-site pair where the source load in the water column is stopped and accumulated water column and sediment concentrations are simulated over time. The recovery period begins after the release period and is simulated for 100years. Fig. 5 shows the concentrations of each nanomaterial divided by the initial concentration at the start of the recovery period (C/C_0) over time for each site. Again, the midstream segment is used for river simulations. The general trend in the recovery scenario simulations is that systems with higher residence times and deeper layers take longer to recover. For all nanomaterials, concentrations in the deep sediments during the recovery period exceeded peak concentrations of the release period in the two lakes. This occurs because the deep sediment layers are still adjusting at the end of the loading period, accumulating heteroaggregated nanomaterials through the slow burial of surface sediments. If the loading period was simulated until concentrations reached steady-state (static or

dynamic) in the deep sediments, concentrations would likely be higher than those reached in the current recovery period and would behave similarly to other layers during a recovery period. Fig. 6 displays the time in years for nanomaterials to recover within each layer and site.

3.4.1. MWCNT—MWCNT in the water column recovered by 90% within two years for all sites except Lake Barco, which took 30years to reach 50% recovery. Surface sediment recovery (90%) ranged from 1 to 12years in the rivers and 37–45years to reach 50% recovery in the lakes. Lake Waccamaw took the longest to recover in the surface sediments (45years). Only Brier Creek reached 50% recovery in the deep sediments after 43years.

3.4.2. GO-rGO—All sites reached 90% recovery in the water column from initial GO concentrations within a year. GO concentrations in the surface sediments recovered by 50% within 39 and 45years in Lake Barco and Lake Waccamaw, while taking less than a year in Yadkin River. No sites recovered by 50% in the deep sediments within the 100-year recovery period. rGO in the water column recovered by 90% within two years except for Lake Barco, which didn't reach 50% recovery within the 100-year recovery period for any layers. Surface sediment recovery ranged from 1 to 12years (90%) in rivers and 51years to reach 50% recovery in Lake Waccamaw. Only Brier Creek reached 50% recovery in the deep sediments after 42years.

3.4.3. Overall trends—In systems with outflow, there is a rapid recovery in the water column for all nanomaterial types. Recovery time in the sediments of each site are consistent for all nanomaterials except for Lake Barco, in which a 50% recovery time varies from 39 to 100years for GO and rGO. This can be explained by the high initial concentrations in the water column, which are only be removed by settling and eventual burial through the sediments. For river sites, recovery time in each layer increases with distance from the loading source.

3.5. Mass flows by period

Fig. 7 shows the nanomaterial mass, in grams per day, leaving and entering each segment layer of Lake Waccamaw at a point in time during the loading period. Similar mass flows during the loading and recovery period are shown for the rest of the systems in Figs. SI 8–9. Mass per time values are from a snapshot during each period, year 49 of the loading period and year one of the recovery period. These distributions are not necessarily at steady state and are simply meant to describe how mass moves through the system at a given point in time for each period.

3.5.1. Loading period—During loading period, free nanomaterials make-up the majority (99%) of the mass for all site system pairs. MWCNT and GO mass in river systems was lost almost entirely to advection (99%), whereas approximately 60% of rGO mass was lost to advection in the headwater segments and increased moving downstream. Lake Waccamaw lost 99% of MWCNT mass by advection, while GO and rGO losses were 15% and 29%. Interestingly, mass loss to burial in Lake Waccamaw is <1% for all nanomaterials as most of the mass is accumulated in the water column as free phase. In Lake Barco, having

no outflow, nanomaterials are removed completely by settling followed by burial. In the lakes, rGO mass produced by the phototransformation of accumulated GO in the water column exceeds the mass of GO being loaded into the system. The river systems had too short of a residence time for rGO formation to be significant.

3.5.2. Recovery period—In the recovery period, free phase mass of all nanomaterials drops rapidly in river segments while decreasing slowly for lakes. Even after free phase nanomaterials are completely removed in the river systems, advective loss remains the dominant means of removal from the overall system. In the headwater segments, Yadkin River nanomaterial mass loss due to burial increases to approximately 24% and Brier Creek mass loss of MWCNT and rGO increases to approximately 50%. Differences in observed trends between Brier Creek and Yadkin River downstream segments are likely due to differences in solids parameterization of each model. Additionally, within each river model, variations in segment residence time as well as dilution from tributary inflows affect solid settling rates and therefore longitudinal trends in nanomaterial concentrations. The Brier Creek model assumes uniform sediment density and inputs of suspended sediment concentrations into the water column. Yadkin on the other hand, has four sample collection sites distributed evenly throughout the system providing a more resolved spatial domain. The differences in parameterization, due to constraints of available data, resulted in differences in solid dynamics over the length of the stream between the two systems. Both rivers see an increase in nanomaterial mass in segments moving downstream. Brier Creek, with a uniform solids parameterization, saw a steady gradual decrease in mass removed by burial moving away from the source. Yadkin River showed the same overall decreasing trend, but with more variability from segment to segment and a much steeper reduction in burial compared to the headwater segment.

Free GO mass drops quickly for all systems during the recovery period which also reduces the production of rGO. Even in Lake Barco, where there is no advective loss, free GO mass remains low relative to free rGO in the loading period and is depleted quickly by phototransformation in the recovery period. Except for advection, mass flows remain similar between loading and recovery periods for GO and rGO. During the recovery period the Yadkin River, which simulates MWCNT as a solid, shows a drop in mass flow ranging from one to three orders of magnitude.

4. Conclusions

The rising global production of nanomaterials increases the risk of exposure in the aquatic environment. In the absence of efficient analytical methods for detecting carbon-based nanomaterials in environmental matrices, fate and transport models are needed to understand how these materials behave in aquatic ecosystems. The physical and chemical properties of natural waters affect the stability of these materials suspended in the water column as well as their heteroaggregation and phototransformation rates. Residence time of a waterbody plays a critical role in the maximum accumulated concentrations as well as the persistence of these nanomaterials.

The objectives of this study were to gain a better understanding of the behavior of carbon-based nanomaterials in different aquatic environments. We simulated a hypothetical loading of nanomaterials into four systems to demonstrate the differences between the exposure concentrations during a loading and recovery period. Heteroaggregation attachment efficiency values were measured for each nanomaterial to parameterize WASP models for each site. The following findings can be attributed to this study:

- Measured α values for carbon-based nanomaterials in the four aquatic environments ranged from approximately 1×10^{-7} to 1×10^{-5} , well outside of the sensitive domain of this parameter. This suggests that there is potential to use estimations of α for carbon-based nanomaterials as opposed to site-specific measurements. The exception to this was GO in Brier Creek in which no heteroaggregation was observed. Additionally, MWCNT were not suspendable in Yadkin River and Lake Barco due to low DOC concentrations. More α measurements are needed both spatially and temporally to better understand these results.
- Systems with longer residence times (lakes vs. rivers) accumulate more nanomaterials in the sediments, the exception to this being when MWCNT was simulated as a solid. Additionally, lakes accumulated higher concentrations of rGO compared to GO whereas rivers had the opposite result.
- Over 99% of nanomaterial mass moves through systems of high and low residence times without being heteroaggregated and deposited into the sediments. This means that concentrations will accumulate downstream in river systems to reservoir or ocean endpoints and can persist in free phase in the water column for extended periods of time.
- While most of the nanomaterial mass exists in the free phase, concentrations accumulate in sediments over time. Given long time periods, concentrations in the sediments can accumulate substantially. Simulations provide recovery periods of 37+years for lakes and 1–4years for rivers to reduce sediment nanomaterial concentrations by 50% suggesting that carbon-based nanomaterials have the potential for long-term ecological effects in the sediments. Variations in temporal and spatial resolution of data inputs could have significant effects on nanomaterial persistence throughout river systems. Further research is needed to determine the sensitivity of physical and chemical parameters on nanomaterial concentrations in each system. Dynamic flow and solid concentrations could provide finer spatial and temporal resolution, potentially showing nanomaterial accumulation hotspots in river systems as well as seasonal nanomaterial mass fluctuations in sediments and surface waters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
Site map with location of four modeled ecosystems. (A) Brier Creek, GA (B) Lake Waccamaw, NC (C) Lake Barco, FL (D) Yadkin River, NC.

Fig. 2. Conceptual model for A) MWCNT simulations and B) GO-rGO simulations. Model processes include (1) advective flow, (2) heteroaggregation, (3) particulate settling, (4) particulate resuspension, (5) burial, (6) light attenuation, and (7) phototransformation. Heteroaggregation between GO and suspended solids occurs in all but the Brier Creek model.

Fig. 3. Accumulation of MWCNT, GO and rGO in water column, surface sediment, and deep sediment layers at the sites during the 50-year loading period.

Fig. 4.

Mass Fractions of MWCNT, GO and rGO in each segment of the four systems. Lines represent the mass fractions of nanomaterial in the water column (WC), surface sediments (SS), and deep sediments (DS). Mass fraction refers to the fraction of total nanomaterial in each scenario in all layers within a segment. GO and rGO fractions are relative to the total mass of GO and rGO.

Fig. 5. GO, rGO and MWCNT C/C_0 over time in all sites during the recovery period. The midstream segment is displayed for Brier Creek and the Yadkin River. Dotted line represents the initial concentration at the start of the recovery period.

Fig. 6.

Time in years to reach 50% and 90% initial recovery concentrations of nanomaterials in each system. Recovery of each nanomaterial is shown in the water column (WC), surface sediments (SS), and deep sediments (DS).

Fig. 7. Mass flow snapshot of total MWCNT, GO, and rGO in Lake Waccamaw 49 years into the loading period.

Table 1

Site specific properties for GO, rGO, and MWCNT. DOC, pH, and cationic strength refer to values from site specific water samples used to measure alpha.

Natural Water	Nanomaterial	D_h (nm)	α ($\times 10^{-5}$ 1/d)	pH	DOC (mg/L)	Cationic Strength (mM)
Lake Waccamaw	GO	466 ± 11.1	1.74	6.60	18.2	1.09
	rGO	763 ± 77.9	0.887	6.60	18.2	1.09
	MWCNT	309 ± 10.4	0.261	6.60	18.2	1.09
Yadkin River	GO	462 ± 71.6	1.04	6.70	3.31	1.29
	rGO	920 ± 35.6	1.38	6.70	3.31	1.29
	MWCNT	2170 ± 552	-	6.70	3.31	1.29
Lake Barco	GO	393 ± 7.34	0.01	5.40	1.55	0.395
	rGO	681 ± 30.4	0.04	5.40	1.55	0.395
	MWCNT	5010 ± 2260	-	5.40	1.55	0.395
Brier Creek	GO	509 ± 2.70	-	6.40	5.58	1.30
	rGO	689 ± 17.3	0.0245	6.40	5.58	1.30
	MWCNT	189 ± 6.40	0.104	6.40	5.58	1.30

Table 2

Summary of site physical and chemical properties. TSS, flow, and DOC values represent average concentration of all segments. Average depth and burial for all segments are shown here for each site.

Site	TSS (mg/L)	Depth (m)	DOC (mg/L)	Residence Time (d)	Burial Rate (cm/yr)	Flow (m ³ /s)
Lake Waccamaw	10	2.3	6.0	370	0.0078	2.6
Lake Barco	2.5	4.0	6.0	-	0.037	-
Yadkin River	21	3.8	5.0	3.1	0.11	53
Brier Creek	18	1.7	7.0	2.4	0.43	8.1

Table 3

Simulated maximum concentrations (ng/L, water, and ng/kg, sediments) during 50-year loading period for each nanomaterial and site pair.

Location	Layer	MWCNT	GO	rGO
Barco	Water Column	5.0×10^3	1.1×10^4	2.1×10^6
Barco	Surface Sediments	9.7×10^8	2.3×10^3	1.3×10^6
Barco	Deep Sediments	9.6×10^7	2.2×10^2	8.2×10^4
Brier	Water Column	170	170	2.0
Brier	Surface Sediments	4.9	-	4.2×10^{-3}
Brier	Deep Sediments	2.9	-	2.5×10^{-3}
Waccamaw	Water Column	440	77	220
Waccamaw	Surface Sediments	2.3×10^4	1.6×10^4	3.1×10^4
Waccamaw	Deep Sediments	230	180	340
Yadkin	Water Column	24	24	0.24
Yadkin	Surface Sediments	2.3×10^4	5.2	3.7×10^{-2}
Yadkin	Deep Sediments	4.9×10^3	1.1	6.2×10^{-3}