MODELING ENGINEERED NANOMATERIALS (ENMS) FATE AND TRANSPORT IN AQUATIC ECOSYSTEMS

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Abstract. Under the Toxic Substances Control Act (TSCA), the Environmental Protection Agency (EPA) is required to perform new chemical reviews of nanomaterials identified in pre-manufacture notices. However, environmental fate models developed for traditional contaminants, like pesticides or hydrophobic organic chemicals, are limited in their ability to simulate the environmental behavior of engineered nanomaterials (ENMs) due to incomplete understanding and quantification of the processes governing ENM distribution in the environment.

We have updated the Water-quality Analysis Simulation Program (WASP), version 8, to incorporate nanomaterials as an explicitly simulated state variable. WASP8 now has the capability to simulate ENM fate and transport in surface waters and sediments using heteroaggregation ($_{TTT}$), the kinetic process governing the attachment of ENMs to particles and the dominant process of ENMs in an aquatic system.

Unlike dissolved chemicals, which use equilibrium partition coefficients, $_{TTT}$ consists of a particle collision rate and an attachment efficiency (α_{het}) that generally act as a one direction process. To demonstrate, we used a derived T_{TTT} value from sediment attachment studies to parameterize WASP for simulation of multiwalled carbon nanotube (MWCNT) transport in Brier Creek, a coastal plain river located in east-central Georgia, USA and a tributary to the Savannah River. Simulations using a constant MWCNT load of 0.1 kg d^{-1} in the uppermost Brier Creek water segment showed that aqueous MWCNTs were present predominantly in the Brier Creek water column, with decreasing concentrations in segments moving from the source. MWCNTs accumulated in sediments attached to different naturally occurring particulates and showed a general increase in concentration in segments moving from the source.

Additionally, simulations adjusting experimentally determined T_{TTT} by an order of magnitude had little effect on MWCNT concentrations in the water column and sediments in Brier Creek. With the increasing production of ENMs, the development of WASP8 for ENMs provides a powerful tool for investigating ecological exposure to these emerging contaminants.

INTRODUCTION

Nanoparticles in the Environment

The unique electronic, mechanical, and structural properties of ENMs have led to rapid increases in their production[1-3]. There are currently more than 1,600 consumer products reported to contain nanoscale materials; the use of carbon-based ENMs (fullerenes, carbon nanotubes (CNTs) and graphene family materials) in these products trails only nano-scale silver and titanium[4]. As more ENMs are produced and utilized in commerce, the potential for either permitted or accidental releases increases; concomitantly, the potential for human and ecological exposures also increases[5,6].

Research on the effects of nanomaterial exposure to environmental and human health is still incomplete and ongoing. These potential exposures underscore the importance of developing models for simulating ENM transport and transformation in the environment. However, environmental fate models developed for traditional contaminants are limited in their ability to simulate ENMs' environmental behavior by incomplete understanding and representation of the processes governing ENM distribution in the environment and by scarce empirical data quantifying the interaction of ENM with environmental surfaces. The purpose of this manuscript is to describe the redesigned architecture of the Water-quality Analysis Simulation Program (WASP) to allow for the simulation of ENMs and present a case study in a real aquatic ecosystem.

WASP8

WASP is a dynamic and spatially resolved mechanistic, differential mass balance fate and transport modeling framework for environmental contaminants in surface waters and sediments. WASP's interface allows the user to construct the model design appropriate for the system of interest, in one, two, or three dimensions. WASP also allows for the time varying processes of advection, disper-

sion, point and diffuse mass loading, boundary conditions, and boundary exchange. Hydrodynamic and sediment transport models can be linked to WASP, or the user can use the algorithms within the WASP framework.

WASP is one of the most widely used water quality models in the USA and throughout the world. WASP has been applied in the development of Total Maximum Daily Loads (TMDLs) [7, 8]; simulation of nutrients in Tampa Bay, FL [9]; and development of remediation strategies for mercury in the Sudbury River, MA [10, 11]. WASP8 is an enhancement of the original WASP developed in the 1980s [12-14]. WASP8 contains two modules: the Advanced Eutrophication (nutrients) module and the Advanced Toxicant module. The focus of this manuscript will be on the Advanced Toxicant module with specific attention given to nanomaterial attachment kinetics.

Particle Attachment

Sorption is the process of attachment or detachment of a contaminant onto a solid material[15,16]. Surface waters contain abundant concentrations of suspended solids (e.g., silt, clay and particulate organic matter), and sorption is an important process affecting the fate and transport of contaminants in aquatic ecosystems. Sorption occurs when the freely suspended contaminant attaches to the surface of a solid. Desorption is the reverse process, the detachment of a sorbed molecule from the solid to the aqueous or gaseous phase.

Sorption is modeled assuming either an equilibrium or a kinetic model. In an equilibrium model, it is assumed that sorption occurs very rapidly and steady state is reached instantaneously. If a kinetic model is used, then the processes are simulated as two competing reactions.

One of the specific features of WASP8 is the introduction of the state variable class NANOC, for nanomaterials (nanochemicals). Both the chemical and nanochemical state variables can simulate kinetic particle attachment in WASP8. The chemical state variable can be modeled with the processes of equilibrium kinetics using partition coefficients and the newly added process of kinetic sorption. Nanomaterials instead, are governed by the kinetic process of heteroaggregation.

Heteroaggregation is the process in which ENMs collide and stick to particulate matter based on three separate collision processes [17-19]. The overall heteroaggregation rate is defined by:

$$(1) \qquad k_{het} = \alpha_{het} \, k_{coli} \, N^{SPM}$$

where α_{het} is the collision efficiency or the probability that an ENM will stick to a suspended solid particle in the event of a collision (a dimensionless parameter that ranges between 0-1 and must be experimentally measured for a specific system), k_{coli} is the rate of collision between two particles in units of volume per day:

$$(2) \qquad k_{coli} = \frac{2 k_B T_{water} (r_{ENM} + r_{SPM})^2}{3 \mu_{water}} + \frac{4G}{3} (r_{ENM} + r_{SPM})^3 + \pi (r_{ENM} + r_{SPM})^2 \left(v_{set}^{ENM} - v_{set}^{SPM} \right)$$

where k_B is the Boltzmann constant (1.38×10^{-23} JK^{-1}), T, μ and G are the absolute temperature (298 K), dynamic viscosity (1.002 mPa·s) and the shear rate of water ($10\ s^{-1}$), respectively. r_{ENM}, r_{SPM}, and v^{set}_{SPM} are the radii and settling velocities of ENMs and suspended particulate matter (SPM), respectively.

The rate of collision between ENMs and particulate matter is dependent on three processes: Brownian motion (perikinetic aggregation), fluid motion (orthokinetic aggregation) and differential settling. Settling velocity is calculated using Stokes' law:

$$(3) \qquad v_{set}^{particle} = \frac{2g(\rho_{particle} - \rho_{water})}{9 \mu_{water}} r_{particle}^2$$

and where N^{SPM} is the number of suspended particles per unit volume:

$$(4) \qquad N^{SPM} = \frac{C^{SPM}}{\frac{4}{3} \pi r_{SPM}^3 \, p_{SPM}}$$

where C^{SPM} is the concentration of suspended particles. We can assume the heteroaggregation rate can be described by a first-order rate constant because the ratio of naturally occurring suspended particles to ENMs is so high.

METHODS

Study Area

Brier Creek is a coastal plain river located in east-central Georgia, USA and a tributary to the Savannah River (Figure 1). The stream is characterized by sandy substrate and relatively low slope. Brier Creek has a residence time of about two and a half days from the headwaters to the USGS gage at Millhaven, GA.

Estimating Alpha

Sediment from Brier Creek was collected and characterized for particle size distribution, mineralogical composition and organic carbon content. Brier Creek water was analyzed for major occurring ions by ICPS-MS, for particulate organic matter (POM, suspended organic materials retained on 0.45 μ filter) and DOC content. MWCNTs, purchased from CheapTubes Inc., were dispersed in the Brier Creek water samples and used to experimentally measure an average alpha for Brier Creek using methods from a previous study (Figure 2).[20]

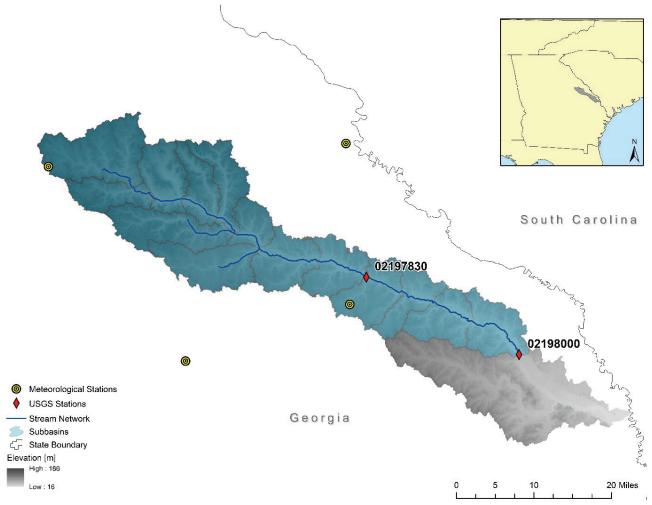

Figure 1. Site map and model domain, Brier Creek, GA, USA

WASP Model

The Brier Creek WASP model was created using the WASP Model Builder tool in BASINS. A model of the Brier Creek watershed upstream from USGS gage 02198000 (Brier Creek at Millhaven, GA) was created for the Hydrologic Simulation Program - FORTRAN (HSPF) to predict streamflow. Watershed delineation was performed in BASINS using a 10-m National Elevation Dataset (NED) and spatial threshold of 96 km^2. The final Brier Creek watershed study area totaled 1,709 km^2 containing 3% impervious and 97% pervious surface area.

This model was divided into 14 sub-basins including two tributaries and 12 sub-basins on the main stem. Sub-basin areas ranged from 50-130 km^2. An NHDPlus (version 2) Flowline layer was simplified and then divided into sections for each of the 14 HSPF sub-basins. The model consisted of 14 longitudinal segments, each containing a water column, surface sediments, and subsurface sediments (deep sediments) layer, for a total of 42 segments. The Flowline shapefile contained physical data for each of the WASP segments.

Solids were modeled using USGS suspended-sediment concentration (SSC) data from stations 02197830 (Brier Creek near Waynesboro, GA) and 02198000 (Brier Creek at Millhaven, GA). Using solids ratios from 02198000 and a porosity of 0.8[21] we calculated initial conditions in the sediments for sand, silt, and clay. Boundary conditions for silt and clay were calculated by averaging SSC data for all sample dates from station 02197830 and partitioning based on the ratios in the sediments. These concentrations agreed with a USGS report on Georgia streams[22].

POM was calculated using data downloaded from EPA's STOrage and RETrieval (STORET) database. Total organic carbon (TOC) measurements from Georgia Environmental Protection Division (GAEPD) stations 1012801 (Brier Creek at SR 56 near Waynesboro) and 1013001 (Brier Creek – Millhaven) were combined to give an average POM of 6.68 mg L^{-1} for the sample period. Settling rates were calculated using Stokes' law and resuspension was set at 2.0 x 10^{-5} for all solids. Table 1 summarizes solids used in the Brier Creek WASP model.

Sand, silt, clay and POM were simulated for 1000 years until steady state conditions were reached in the deep sediment segments. A 300 kg d^{-1} load of sand was added to surface sediment segments to reach sediment concentration ratios similar to USGS 02198000. These steady state concentrations were used as initial conditions for the ENM scenario.

Calibrated streamflow simulated by HSPF was averaged by segment for the calibration period 1/01/1992-12/31/1999. The model has three boundary conditions including the headwaters of Brier Creek and two tributaries, Brushy and Reedy Creeks (Figure 3).

A 0.1 kg d^{-1} load of MWCNTs was added to the headwater boundary of Brier Creek to simulate a point source scenario at steady state. Using water and sediment samples from Brier Creek, it was determined that the average $_{TTT}$ attachment efficiency (α_{het}) was 1.04 x 10^{-6} with a 95 percent confidence interval of ±1.65 x 10^{-2}. In order to model attachment phases of a nanoparticle in WASP8, a separate nanochemical variable for each phase was created and linked mechanistically.

Heteroaggregation is the process acting on phases, moving from freely suspended nanoparticles to attachment to either a silt, clay or POM particle. This is a one directional reaction with nanoparticle-solid phases adopting the settling/resuspension rates of the solid to which they are attached. Sand is modeled only as a sediment substrate and not considered in the $_{TTT}$process due to its high settling rate. WASP8 simulates the concentrations of each phase separately. Freely suspended nanoparticles were modeled with a diameter and settling velocity of 150 nm and 1.03 x 10^{-3} m d^{-1}.

Table 1. Solids modeled in the Brier Creek WASP model. Initial conditions are based on SSC data from USGS gage 02198000. Boundary conditions and particle diameters are based on SSC data from USGS gage 02197830.

Solid Type	Diameter [mm]	Initial Cond [mg L^{-1}]	Boundary Cond [mg L^{-1}]	Settling Rate [m d^{-1}]	Density [g cm^{-3}]
Sand	4.031	498,200	0	0	2.65
Silt	0.006	5,300	1.93	1.40	2.65
Clay	0.002	26,500	9.65	0.16	2.65
POM	0.005	0	6.68	0.25	1.50

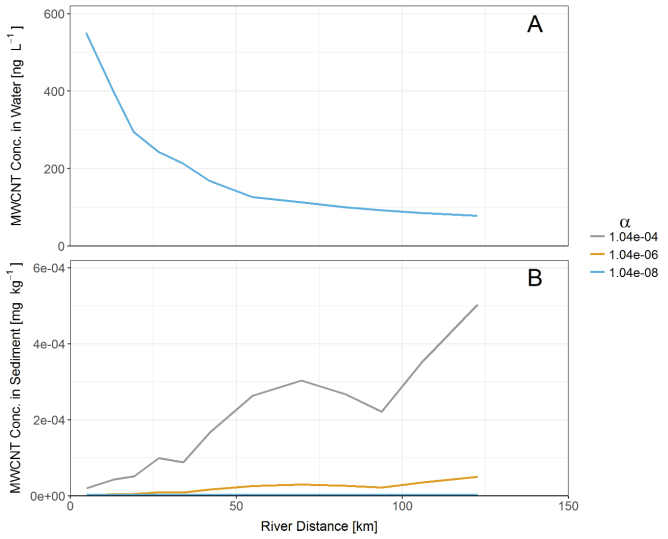

Figure 2. Total MWCNT concentration in the (A) water column and (B) surface sediments versus distance for different α_{het} values.

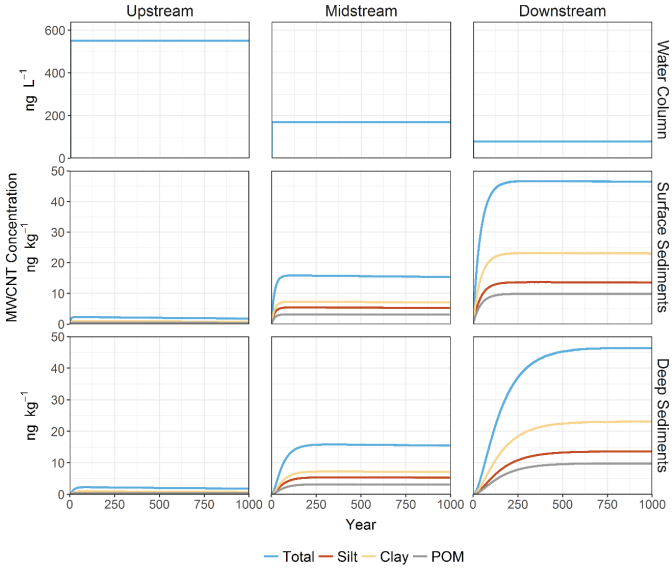

Figure 3. MWCNT concentrations over time [years] in the water column, surface sediments and deep sediments.

RESULTS AND DISCUSSION

Steady state simulated concentrations of particulates and MWCNT using an average α_{het} (1.04 x 10^{-6}) for Brier Creek are presented in Figure 4. Simulations used constant boundary and flow conditions while the system itself is dynamic: particulates settle and re-suspend. Total MWCNT in the water column reached steady within the first year, decreasing with distance from 551 ng L^{-1} at the source segment (0 – 9.7 km) to 66 ng L^{-1} in the last segment (113 – 132 km).

This decrease in concentration with distance is mainly due to dilution from incoming tributaries. MWCNT in the sediments gradually increase with distance and accumulate in the downstream segment. Total MWCNT concentrations increase from 1.8 - 46.4 ng per kg of sediment in both the surface and deep sediments. This reflects kinetics of particle attachment moving downstream; as residence time increases, there is more time for attachment to occur and deposition of sorbed MWCNTs to the sediments. Sediment layers accumulate sorbed MWCNT with clay > silt > POM.

Cumulative probability distributions have been used to describe CNT ecotoxicity in fresh water, and it has been reported that less than 5% of the surveyed species would be affected at concentrations < 3.5 mg L^{-1}.[23] In a study on the effects of MWCNT dosing at 15 and 30 mg L^{-1} on algae growth, it was observed that humic acid significantly reduced MWCNT induced oxidative stress as well as MWCNT cell internalization.[24] Observed MWCNT stability in Brier Creek water is likely due to the coating of MWCNTs by Brier Creek DOC, which would also lead to a decrease in algae oxidative stress and cell internalization. The MWCNT loadings simulated in this study would likely have a minimal effect on water column biota.

Varying α_{het} by an order of magnitude above and below (1.04 x 10^{-4} and 1.04 x 10^{-8}) the average measured value for Brier Creek (1.04 x 10^{-6}) had little effect on MWCNT concentration in the water column and sediments.

CONCLUSIONS

The results of this study demonstrate the ability of WASP8, an enhanced version of WASP, to model the fate and transport of ENMs using newly added kinetic sorption processes. We simulated a hypothetical point source release of MWCNTs in the headwaters of a coastal plains watershed using average observed water column and sediment data. Ongoing research will investigate the fate and transport of ENMs in different ecosystems with different characteristics and water chemistry. Further research will also incorporate dynamic streamflow and sediment data into an aquatic ecosystem.

Disclaimer. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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