

Simulation of the Environmental Fate and Transformation of Nano Copper Oxide in a Freshwater Environment

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Cite This: *ACS EST Water* 2022, 2, 1532–1543

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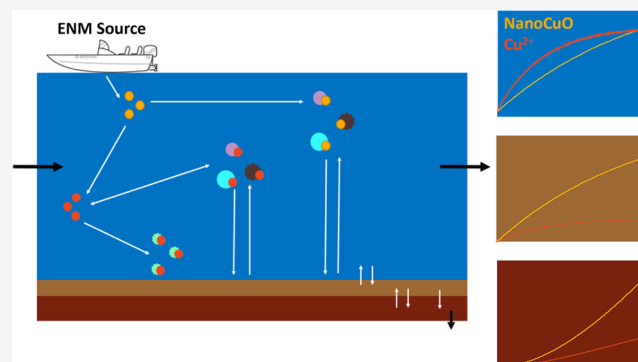
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ABSTRACT: Production of engineered nanomaterials (ENMs) has rapidly increased, yet uncertainty exists regarding the full extent of their environmental implications. This study investigates the fate, transformation, and speciation of nano copper oxide (nanoCuO) released into Lake Waccamaw, North Carolina, over 101 years. Using the Advanced Toxicant module of the Water Quality Analysis Simulation Program (WASP8), we assessed the accumulation and mass proportions of nanoCuO and Cu^{2+} (the product of nanoCuO's dissolution) in the water column and sediments. Our simulations suggest that when nanoCuO is released into Lake Waccamaw, the highest concentrations of both nanoCuO and Cu^{2+} are found in the surface sediments, followed by the subsurface sediments and the water column. Simulating different heteroaggregation attachment efficiencies of nanoCuO suggested that increases in attachment efficiency increased nanoCuO concentrations and mass proportions in the water column and sediments, while Cu^{2+} exhibited the opposite trends. After 101 years, most nanoCuO in the sediments was attached to particulate organic matter and clay particles at all attachment efficiencies, while low attachment efficiency slowed aggregate formation in the water column. Our results highlight the influence that heteroaggregation has on the behavior of nanoCuO inputs and suggest the potential for legacy contamination of nanoCuO and Cu^{2+} in sediments.

KEYWORDS: WASP, environmental modeling, nanocopper, nanomaterials, freshwater



1. INTRODUCTION

The production and use of engineered nanomaterials (ENMs) have rapidly increased over the past few decades, and have subsequently boosted ENM release into the environment.^{1–3} The Nanotechnology Consumer Products Inventory currently lists over 1800 products containing ENMs, which are materials that have at least one dimension between 1 and 100 nm in length.^{4,5} ENMs' high surface area-to-volume ratios and novel physical characteristics promote their widespread use across many different applications, including electronics, medicine, textiles, cosmetics, and protective coatings.^{5–7} Despite the growing ENM market, a large amount of uncertainty exists regarding the full extent of ENMs' impact on environmental and public health.^{3,8}

Copper, which has been found to have toxic effects on fish, shellfish, and benthic organisms,^{9–13} has been a key component of antifouling products used in aquatic environments, such as boat-bottom paints and lumber treatments.^{14,15}

When ingested, copper produces reactive oxygen species (ROS) within organisms. ROS induce oxidative stress in these organisms, which can cause genotoxic and/or cytotoxic damage.^{9,16,17} The tendency for copper from antifouling products to persist in environmental systems prompted the need for a safer, more effective alternative. Copper-based

ENMs have been used as an alternative aquatic biocide and have been identified as superior products due to their slower release from/longer lifespan on boat surfaces compared to traditional copper paints.¹⁸ Oxidized copper-based ENMs, such as nano copper oxide (nanoCuO), are expected to enter aquatic environments in higher volumes than their nonoxidized metallic forms due to their widespread use in antifouling surface treatments, as well as metallic nanocopper's tendency to oxidize over time.^{2,19–21} NanoCuO is particularly toxic compared to other ENMs, especially toward fish and other aquatic organisms.^{2,10,17,22} Dissolution of nanoCuO produces copper ions, whose toxic properties mean that nanoCuO can be associated with multiple routes of toxicity.^{5,23} Dissociated copper ions, which primarily exist in surface waters in their cupric form (Cu^{2+}), go on to form complexes and/or solids by reacting with a number of other compounds found in surface waters and sediments, including organic matter, sulfates,

Received: April 7, 2022

Revised: July 28, 2022

Accepted: July 29, 2022

Published: August 12, 2022



sulfides, hydroxides, and carbonates.^{12,24} Copper ions will continue to cycle in the environment because metals are conserved in environmental systems, unlike carbon-based ENMs, which are vulnerable to biological degradation.^{24–26}

A primary goal of the United States Environmental Protection Agency's (US EPA's) Toxic Substances Control Act (TSCA) is to assess the impact of new and existing chemicals on public and environmental health.²⁷ The expanding copper-based ENM market has increased the need for comprehensive studies on their fate, transport, and transformations. Due to the uncertainty surrounding nano-CuO's environmental impact, as well as the underdeveloped status of ENM field detection methods, studies targeting nanoCuO have primarily taken place in the laboratory setting.^{20,22,28–31} Laboratory studies provide valuable information about the processes governing the behavior of nanoCuO. However, laboratory experiments often use concentrations higher than those found in the environment.²⁰

Environmental modeling allows for large-scale investigations of physical and chemical phenomena that cannot be measured in field/laboratory studies and may help regulatory agencies make informed policy decisions to better protect the environment.³² The ability to analyze theoretical scenarios based on authentic environmental systems, as well as the freedom to extend that analysis for durations far longer than those possible in empirical experiments, contribute to the immense value of environmental models. The Water Quality Analysis Simulation Program (WASP) is a differential mass balance modeling framework that allows users to create dynamic, mechanistic water quality models capable of simulating concentrations in both surface waters and sediments of waterbodies^{33,34} (many of which have become recognized in the literature as “subaqueous soils” due their demonstration of pedogenic processes and their ability to support plant life³⁵). WASP allows users to model the water column and underlying sediments of 1, 2, and/or 3-dimensional systems and can be linked with hydrologic models that capture surrounding watersheds. WASP8 (version 8.32) has recently been updated to include a Eutrophication module, which includes specific biological and chemical variables and processes involved in the eutrophication of surface waters, and an Advanced Toxicant module capable of modeling key processes associated with nanomaterials, such as heteroaggregation and phototransformation. To the authors' knowledge, WASP is one of the few publicly available programs capable of modeling these key nanomaterial processes and allows for the transformation of a nanomaterial into a chemical solute (other nanomaterial models include SimpleBox 4nano,³⁶ NanoFASE,³⁷ and nanoFATE³⁸). WASP has been used to model the fate and transport of both carbonaceous and metallic ENMs throughout all components of aquatic ecosystems, including the water column and sediment layers.^{25,26,34,39–41} This is the first study using WASP to model the fate and transport of nanocopper.

Few studies have modeled nanoCuO in environmental systems,^{28,42} and only one other study to date has modeled both nanoCuO and the products of its dissolution, cupric ions (Cu²⁺).³⁸ In this study, we used WASP8 (version 8.32, <https://www.epa.gov/ceam/water-quality-analysis-simulation-program-wasp>) to model the variables and processes that govern nanoCuO's behavior once released into a freshwater environment (Lake Waccamaw, North Carolina). We chose to model Lake Waccamaw since it is a well-studied system with a level of characterization that is sufficient for our modeling

purposes. Based on the recreational usage patterns of Lake Waccamaw visitors, we targeted 337 recreational boats as a continual source of nanoCuO into Lake Waccamaw, and we evaluated the fate and transport of both nanoCuO and its dissociated Cu²⁺ ions and assessed ecosystem response from a complete removal of its nanomaterial source. Finally, we investigated nanoCuO behavior for different heteroaggregation attachment efficiencies.

2. METHODS

2.1. Study Area. Lake Waccamaw is a freshwater drainage lake in Columbus County, North Carolina (34.3191° N, 78.5000° W). It is the largest natural bay lake on North Carolina's coastal plain, with a surface area of 36 km² and an average depth of 2.3 m, and is surrounded by a flat, wetland-rich landscape.^{40,43} The lake has a relatively neutral pH, ranging from 6.8 to 7.5.^{44,45} Our model incorporates two mechanisms of loss from Lake Waccamaw: advection and burial transport materials across the boundary perimeters of our water column and subsurface sediment compartments, respectively. Lake Waccamaw receives a steady average inflow of 2.6 m³/s, primarily sourced from Big Creek, and drains into the Lake Waccamaw River at the same rate.^{43,46} Sediments in Lake Waccamaw consist of gyttja (mud), peat, and sand and exhibit a burial rate of ~0.075 mm/year.^{46,47} Lake Waccamaw serves as a popular recreational fishing destination for tourists and local residents.

2.2. WASP Model. **2.2.1. Model Structure.** Using the Advanced Toxicant module in WASP version 8.32, we modeled the fate and transport of nanoCuO and Cu²⁺ in Lake Waccamaw from January 1, 2000 to January 1, 2101 (see the [Supporting Information](#) for additional details on model creation). Our study targets the surface waters and sediments of Lake Waccamaw, and thus we did not link our model to any external hydrologic watershed models. Parameters for Lake Waccamaw were based on Avant et al.,⁴⁰ who modeled the environmental fate and transport of multiwalled carbon nanotubes and graphene oxide. The model consists of three well-mixed compartments: the water column (“Water Column;” 2.30 m), a surface layer of aerobic/biologically-active sediments (“Surface Sediments;” 0.02 m), and an underlying layer of anaerobic sediments (“Subsurface Sediments;” 0.18 m), which typically exhibit little to no aerobic biological activity.^{40,48} WASP simulates state variable concentrations in all three model compartments simultaneously. We modeled a total of 10 state variables ([Table 1](#)), including nanoCuO and Cu²⁺ concentrations, dissolved organic carbon (DOC; the primary dissolved ligand involved with copper kinetics²⁴), and both organic (particulate organic matter; POM) and inorganic (sand, silt, clay) particles. In WASP, ENMs are simulated based on principles of colloidal theory.³⁴ Finally, we modeled all potential aggregates resulting from the heteroaggregation of free nanoCuO with viable solid particles (nanoCuO-silt, nanoCuO-clay, and nanoCuO-POM). Due to their rapid settling rate, sand particles do not play an active role in heteroaggregation.²⁶ We also simulated molecular diffusion of Cu²⁺ between the water column and sediments, as well as Lake Waccamaw's inflow and outflow. We acknowledge that Cu²⁺ forms pH/redox-dependent complexes with many compounds found in surface waters, and thus when we refer to Cu²⁺, we are referring to all potential species of Cu²⁺ (rather than the singular, free-floating ion). Additional Lake

Table 1. State Variables and Associated Properties Included in Our Model^a

State variable	Particle diameter (mm)	Density (g/cm ³)	Boundary condition (mg/L)
sand	4.000	2.65	0
silt	0.006	2.65	0.89
clay	0.003	2.65	8.00
POM	0.003	1.5	7.00
DOC	NA	NA	6.00
Cu ²⁺	NA	NA	0
free nanoCuO	9.2×10^{-5}	6.37	0
nanoCuO-silt	0.006	2.65	0
nanoCuO-clay	0.003	2.65	0
nanoCuO-POM	0.003	1.50	0

^aState variable properties for solids and DOC were obtained from Avant et al.³⁵ Free nanoCuO properties were obtained from Miao et al.²⁸ NanoCuO aggregates possess the properties of the particle with which they heteroaggregate.

Waccamaw parameters can be found in the Supporting Information (Tables 1, S1, and S2).

2.2.2. Nanomaterial Load. Approximately 337 boats remain moored in the lake year-round, as the lake does not freeze during the year (T. Hall, personal communication, March 2021). For risk assessment purposes, we assumed that all boats moored in Lake Waccamaw are coated with nanocopper-based boat-bottom paint, which is feasible given the increase in nanocopper antifouling products.¹⁸ Nanocopper-based antifouling paints have been found to leach both nanosized particles and ionic copper.^{15,49} However, under the EPA, TSCA is required to perform new chemical reviews of nanomaterials to regulate the release of materials such as nanoCuO. If nanoCuO is released from boats as Cu²⁺, it no longer falls under TSCA's jurisdiction. To investigate the conservative case for regulation under TSCA, we chose to assume the entirety of the paint load consists of nanoCuO.²⁶ Using our estimate of the number of boats moored in Lake

Waccamaw, an approximation of the wetted surface area of recreational boats in freshwater environments (27.6 m²),⁵⁰ and a measurement of the release rate of nanocopper from antifouling paint from boat bottoms,¹⁵ we calculated a constant nanomaterial load of 0.280 kg nanoCuO/d (see the Supporting Information for more information). While the possibility exists that the nanomaterial load may vary over the course of 101 years, predicting this variation is outside the scope of this study. We chose to simulate a consistent load so that we could focus on the environmental processes governing ENM fate and transport. In addition, we modeled the concentrations of nanoCuO and Cu²⁺ in the water column and sediments resulting from half (0.140 kg nanoCuO/day) and double (0.560 kg nanoCuO/day) our estimated loading rate to account for this uncertainty. Future research targeting the site-specific quantification of nanomaterial loads emitted by boats may be beneficial. To simulate a recovery period for Lake Waccamaw, we removed the nanoCuO load after 50 years and assessed the subsequent accumulation of nanoCuO and Cu²⁺ for the remainder of our study period.

2.2.3. Solids. We simulated 4 types of solid particles in the water column, surface sediments, and subsurface sediments: sand, silt, clay, and POM (Tables 1 and S2). Solid particle concentrations are individual state variables based on user-defined properties (see Table 1). This allows for a dynamic assessment of the behavior of various solid materials throughout the entire duration of the simulation.³⁴ Processes governing the fate and transport of solid particles include advection, sedimentation, resuspension, and burial. Sedimentation and resuspension rates for each particle can be found in Table S3. As solids settle and accumulate in the sediments, WASP's dynamic bed compaction option, with a timestep of 2 days, buries a mass of solids to maintain the initial volume and bulk density of the solids (Supporting Information: Data Set Properties).

2.2.4. Governing Processes. To evaluate the fate and transport of nanoCuO and Cu²⁺ in Lake Waccamaw, through literature review, we identified the predominant processes that

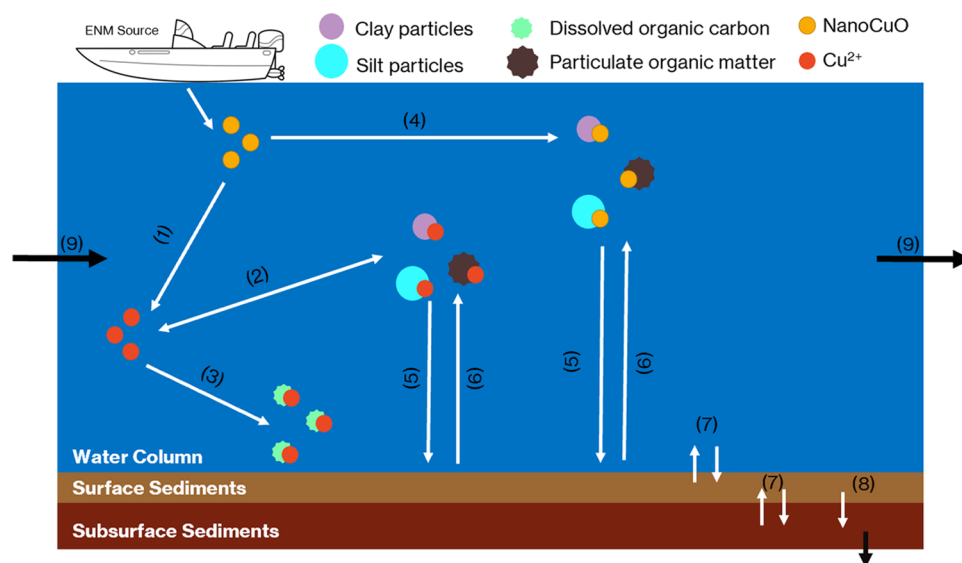
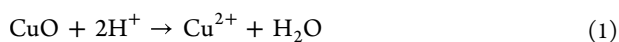


Figure 1. Conceptual model detailing the processes governing the fate and transport of nanoCuO and Cu²⁺ contributed by an engineered nanomaterial (ENM) source. Model processes include (1) dissolution, (2) sorption, (3) complexation, (4) heteroaggregation, (5) sedimentation, (6) resuspension, (7) diffusion, (8) burial, and (9) advection (inflow/outflow). Black arrows represent processes that transport materials out of our model system. Recreational boats serve as the model's nanomaterial source.

govern their behavior in the environment and subsequently translated these processes into our model (Figure 1). We parameterized these processes based on the average pH of Lake Waccamaw (ranging from 6.8 to 7.5^{44,45}), which allowed us to capture the impact pH has on the governing processes without simulating pH directly. These processes include dissolution, sorption, complexation, heteroaggregation, sedimentation, and resuspension (Tables S4 and S5).

2.2.4.1. Governing Processes: Nano Copper Oxide. Four primary processes govern the behavior of nanoCuO once released into the environment: dissolution, heteroaggregation, sedimentation, and resuspension (Figure 1). Once nanoCuO is released into surface waters, it may dissolve to yield Cu²⁺ ions, an irreversible process^{19,20,32} (Table S4).



Given that ENMs are typically outnumbered by naturally occurring ligands in natural waters, heteroaggregation, rather than homoaggregation, governs ENM aggregation kinetics in the environment.^{6,26,38,42,51} Once heteroaggregation occurs, ENMs behave as the particles to which they have aggregated. Heteroaggregation rates are a function of three primary factors: attachment efficiency (α_{het}), collision frequency (k_{coll}), and number of suspended particles (N_{spm}).⁶

$$k_{\text{het}} = \alpha_{\text{het}} \times k_{\text{coll}} \times N_{\text{spm}} \quad (2)$$

Although studies have investigated heteroaggregation of nanoCuO particles,^{17,30} the process is site-specific. While WASP calculates k_{coll} and simulates N_{spm} , α_{het} , which is always between 0 and 1, depends on both site properties, such as pH, ionic strength, and natural organic matter concentration, and nanomaterial properties, such as surface charge and hydrophobicity.^{21,26,52–54} Studies have reported a wide range of α_{het} values for ENMs, ranging from <0.001 to 1.0.^{6,52,55–57} The amount of data available detailing specific α_{het} values for nanoCuO and other nanometals is limited. We chose to use $\alpha_{\text{het}} = 0.1$ for our primary model (“ $\alpha = 0.1$ case”), as we believe it to be an appropriate mid-range value amid the range of potential/probable attachment efficiencies. To address this uncertainty, we also performed two additional simulations using $\alpha_{\text{het}} = 0.01$ (“ $\alpha = 0.01$ case”) and $\alpha_{\text{het}} = 1.0$ (“ $\alpha = 1.0$ case”) to represent a realistic range of α_{het} values and investigate differences in the fate and transport of nanoCuO as α_{het} varies (eqs S3–S5).

Current mathematical models assume that once ENMs heteroaggregate with other particles, the aggregate remains intact, and no further dissolution occurs.^{6,26,34,51} While some laboratory studies have found limited dissolution of nanometals post-heteroaggregation,^{58–61} most suggest that dissolution is inhibited by the heteroaggregation process. Furthermore, the studies do not parameterize the dissolution rates in a way that could be applied to our study. To investigate the impact that the dissolution of heteroaggregates may have on the fate and transport of nanoCuO, we performed a sensitivity analysis. We wanted to evaluate the effects of dissolution post-heteroaggregation using rates slower than the dissolution rate of free nanoCuO, given the likelihood that dissolution would be at least partially slowed or inhibited. To do this, we used an aggregate dissolution rate of 0.01 and 0.1% of our original predicted dissolution rate for free nanoCuO and compared the results to our primary simulation, in which aggregates do not dissolve (Figure S4). We found that while

nanoCuO and Cu²⁺ concentrations slightly changed from our primary simulation, (1) most changes only became evident toward the end of our 101-year simulation, and (2) accumulation trends were similar to our primary simulation (which assumed no dissolution post-heteroaggregation). Due to these findings, along with the lack of parameterization of dissolution of nanometals post-heteroaggregation, we assumed in our model that dissolution of Cu²⁺ from nanoCuO aggregates is negligible.

NanoCuO is assumed to remain suspended in the water column until it attaches to a solid particle.²⁴ Sedimentation and resuspension for ENMs are driven by the behavior of particles to which they aggregate^{6,51} (Table S3). In our model, “total nanoCuO” refers to the sum of free nanoCuO and all nanoCuO aggregates (nanoCuO-silt, nanoCuO-clay, nanoCuO-POM).

2.2.4.2. Governing Processes: Ionic Copper. The behavior of Cu²⁺ in the environment is driven by four processes: complexation, sorption, sedimentation, and resuspension (Figure 1). Cu²⁺ forms stable complexes with a wide variety of natural ligands in aquatic environments, particularly DOC.^{9,12,24,62} We model Cu²⁺ complexation as a function of DOC concentration; while we acknowledge that Cu²⁺ can form a large variety of complexes in aquatic environments, parameterizing the entire profile of natural ligands present in Lake Waccamaw and modeling their complexation with Cu²⁺ was outside the scope of this study (Table S5). Sorption of Cu²⁺ to solid particles is modeled as a bidirectional process.²⁴ Cu²⁺ has a strong affinity for solid particles, and its affinity varies based on particle size¹² (Table S5). Similar to nanoCuO, Cu²⁺ will not settle out of the water column unless attached to a particle. Once sorbed to inorganic (silt or clay) or organic particles (POM), the sedimentation and resuspension rates of Cu²⁺ are driven by the properties of said particles (Table S3). In addition to forming complexes with a variety of natural ligands, Cu²⁺ may also react with compounds to form solid precipitates in aquatic environments. Thus, in our model, “total Cu²⁺” refers to all potential species of Cu²⁺.

One additional process that may govern Cu²⁺ behavior in aquatic environments is sulfidation. Sulfidation takes place in anoxic environments, where anaerobic respiration produces hydrogen sulfides. Cu²⁺ may then react with the resulting hydrogen sulfides to form copper sulfides, effectively sequestering the Cu²⁺ in a solid form (provided redox conditions remain stable).¹² We chose to exclude sulfidation from our model because we believe its impact on our results would be negligible. Due to its warm climate and well-mixed nature, Lake Waccamaw does not undergo thermal stratification, and its water column and surface sediments remain oxic throughout the year. While the subsurface sediments likely reach the anoxic conditions necessary for sulfidation to occur, any form of copper present in the subsurface sediments likely remains buried there and does not transport up to the surface sediments or the water column.

2.2.5. Water Temperature Model. Because water temperature influences ENM collision rate (eq S4), we used WASP8 to simulate Lake Waccamaw’s water temperature explicitly using historical climate data.²⁶ This allowed us to consider seasonal variations in the fate and transport of nanoCuO and Cu²⁺ as a function of water temperature. Using the US EPA’s Hydrologic Micro Services (<https://www.epa.gov/ceam/hydrologic-micro-services-hms>), we obtained solar radiation, air temperature, wind speed, and dew point data for Lake

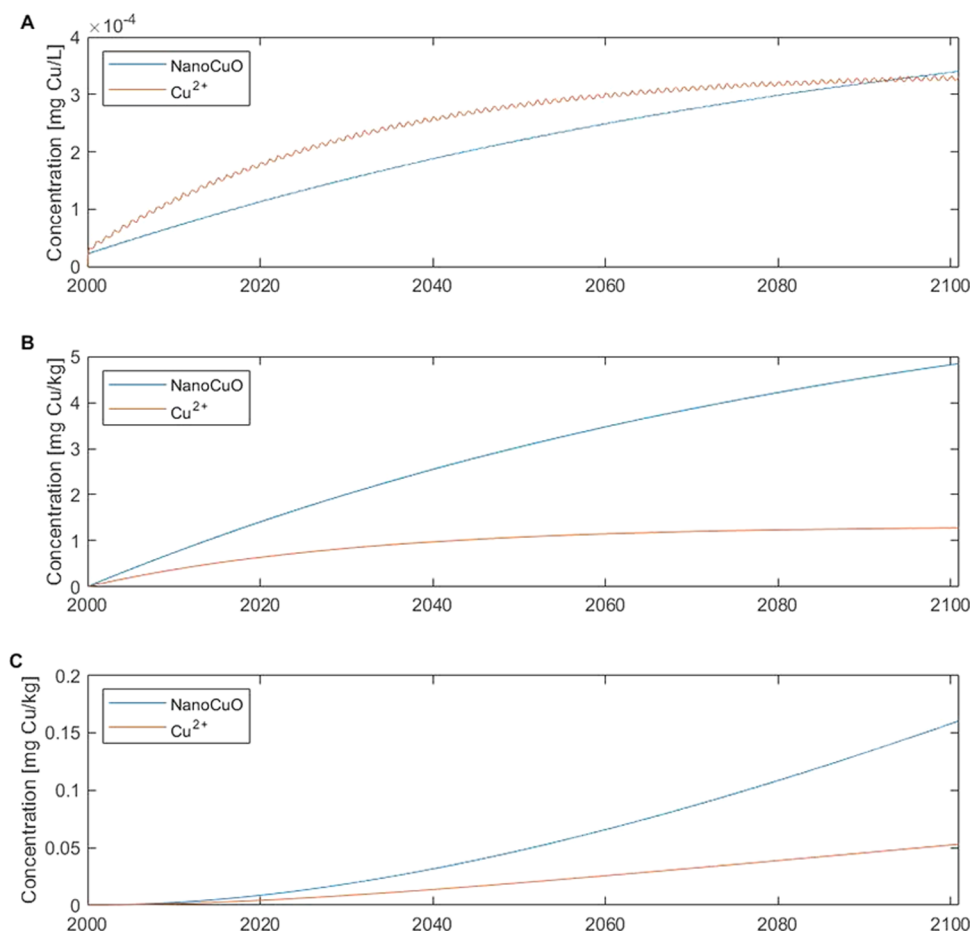


Figure 2. Accumulation of nanoCuO and Cu^{2+} in the water column ((A) water column and sediments (B) surface sediments and (C) subsurface sediments) of Lake Waccamaw between January 1, 2000 and January 1, 2101 for our primary model, where attachment efficiency = 0.1.

Waccamaw for the years 2000–2020 (21 years total).⁶³ We replicated our 21 years' worth of water temperature measurements to create a 101-year time series and added the temperatures as a time function (see the Supporting Information for additional information; Figure S1).

2.3. Mass Load and Proportion Calculations. We calculated the total mass of copper (sum of nanoCuO and Cu^{2+}) leaving Lake Waccamaw via advection by multiplying the water column concentration of nanoCuO and Cu^{2+} at each timestep by the lake's outflow rate ($2.6 \text{ m}^3/\text{s}$). We also calculated the proportion of Cu^{2+} versus nanoCuO relative to the total mass of copper present in the water column, surface sediments, and subsurface sediments, as well as the proportion of each form of nanoCuO (free nanoCuO and nanoCuO aggregates) relative to the total mass of nanoCuO in each model compartment upon the conclusion of our $\alpha = 0.01$, $\alpha = 0.1$, and $\alpha = 1.0$ case simulations. See the Supporting Information for additional information (eqs S6–S8).

3. RESULTS AND DISCUSSION

3.1. Accumulation of NanoCuO and Cu^{2+} . We used WASP8 to simulate the addition of nanoCuO to Lake Waccamaw and assessed the accumulation of total nanoCuO (free nanoCuO and its aggregate forms) and Cu^{2+} (free, complexed, and sorbed Cu^{2+}) in the water column and sediments over the course of 101 years. Figure 2 shows nanoCuO and Cu^{2+} concentrations over the duration of our simulation (January 1, 2000–January 1, 2101) in each of the

model's three compartments ((A) water column, (B) surface sediments, and (C) subsurface sediments). Concentrations of nanoCuO and Cu^{2+} increased in and varied among all model compartments (Figure 2). At the end of our simulation, the highest concentrations of both nanoCuO and Cu^{2+} were found in Lake Waccamaw's surface sediments (4.85 and 1.27 mg Cu/kg), followed by the subsurface sediments (0.16 and 0.05 mg Cu/kg), and the water column (3.40×10^{-4} and $3.31 \times 10^{-4} \text{ mg Cu/L}$). Note that water column and sediment concentrations are reported in different values to best reflect how concentrations would be measured in the field. However, the conversion between mg/L and mg/kg is based on sediment bulk density, which in our system is $\sim 1 \text{ kg/L}$. This allows for a direct comparison among model compartments. Cu^{2+} concentrations initially increased quickly in the water column and surface sediments, with a continually slowing rate of accumulation as the simulation continued (Figure 2). NanoCuO concentrations steadily increased in the water column and sediments for the entire simulation, resulting in nanoCuO concentrations eventually surpassing Cu^{2+} concentrations despite Cu^{2+} 's initial rapid accumulation. NanoCuO concentrations were perpetually higher than Cu^{2+} concentrations in the sediments. Concentrations of both nanoCuO and Cu^{2+} increased slowly for ~ 40 years in the subsurface sediments, then their rate of accumulation increased rapidly for the remainder of our simulation (Figure 2). Sensitivity analysis evaluating nanoCuO and Cu^{2+} concentration variations in response to half and double the nanoCuO loading rate showed

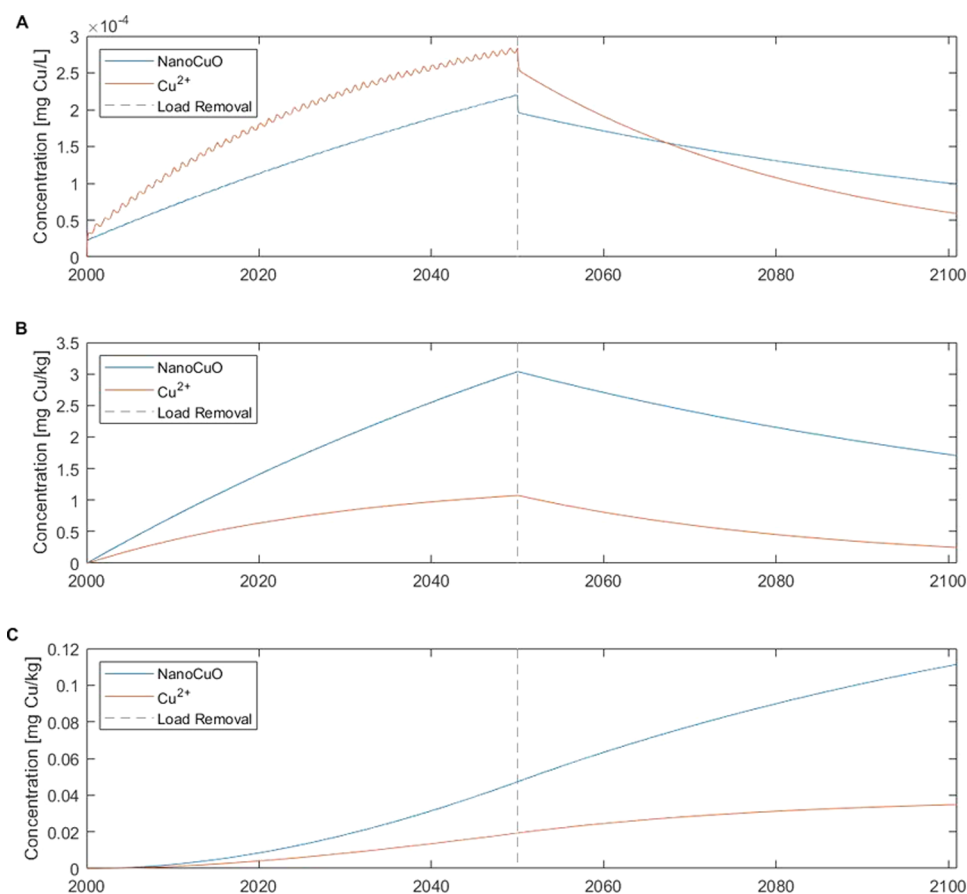


Figure 3. Accumulation of nanoCuO and Cu^{2+} in the water column ((A) water column and sediments (B) surface sediments and (C) subsurface sediments) of Lake Waccamaw during a loading period of nanoCuO (January 1, 2000–December 31, 2049) and a recovery period (January 1, 2050–January 1, 2101). The plots reflect our primary model, where attachment efficiency = 0.1. The dashed gray line represents the time at which we removed the nanoCuO load.

that the model is scaled linearly, and therefore concentrations can be adjusted in response to the loading rate (Figure S3). While WASP simulates nanomaterials internally as number of particles, the output is in mass concentration to allow for meaningful comparisons to regulatory and toxicity thresholds and field measurements (eq S9).

Our results reflect seasonal changes in water temperature. Water column Cu^{2+} concentrations rise in the cooler, winter months (January–March) and fall in the warmer, summer months (July–September; Figure 2). Conversely, upon close inspection of Figure 2, our simulation showed nanoCuO concentrations rising in the summer months (July–August) and falling in the winter months (January–February; see Figure S2 for a detailed illustration of seasonal variation). To the authors' knowledge, this is one of the first studies to model real-time water temperatures alongside the behavior of nanoCuO. Although the variation for nanoCuO is less pronounced than that exhibited by Cu^{2+} , we believe this seasonal variation is driven by the physical processes captured in our model. The collision frequency of particles due to Brownian motion, a key component of heteroaggregation dynamics, is linearly dependent on temperature (eq S4). As temperature increases, nanoparticles collide more frequently with suspended particles, increasing the heteroaggregation rate.⁶ Based on our sensitivity analysis of dissolution post-heteroaggregation (Figure S4), our model assumes that dissolution of nanoCuO heteroaggregates is limited/negligible;

thus, the amount of time available for nanoCuO to dissolve to yield Cu^{2+} decreases in warmer months as heteroaggregation rates increase. This rationale is supported by the elevated concentrations of Cu^{2+} present in the water column during the cooler months when free nanoCuO remains in solution longer and subsequently has more time to undergo dissolution. Increased temperatures may also boost dissolution rates, although few studies have investigated this possibility for nanoCuO. Future research efforts may help improve our understanding of the relationship between temperature and nanoCuO behavior.

Our results suggest that particle attachment of nanoCuO and Cu^{2+} , heteroaggregation and sorption, play a major role in the fate and transport of both forms of copper. Nanoparticles will heteroaggregate quickly with inorganic and organic particles in surface waters.⁴¹ Furthermore, sorption of metal ions such as Cu^{2+} is typical in waters of ambient pH, such as Lake Waccamaw, due to the negative charge of most solids.⁵² Once attached to solid particles, nanoCuO and Cu^{2+} are more likely to sediment out of the water column and accumulate in the sediments.³¹

The tendency for ENMs to accumulate in the sediments of aquatic environments has been noted in other studies. Dale et al.⁵⁶ used WASP7 to assess the dynamics of silver and zinc oxide nanoparticles in a freshwater stream and also observed the highest ENM concentrations in the stream's surface sediments. Dale's model assumes that metal ENMs with a

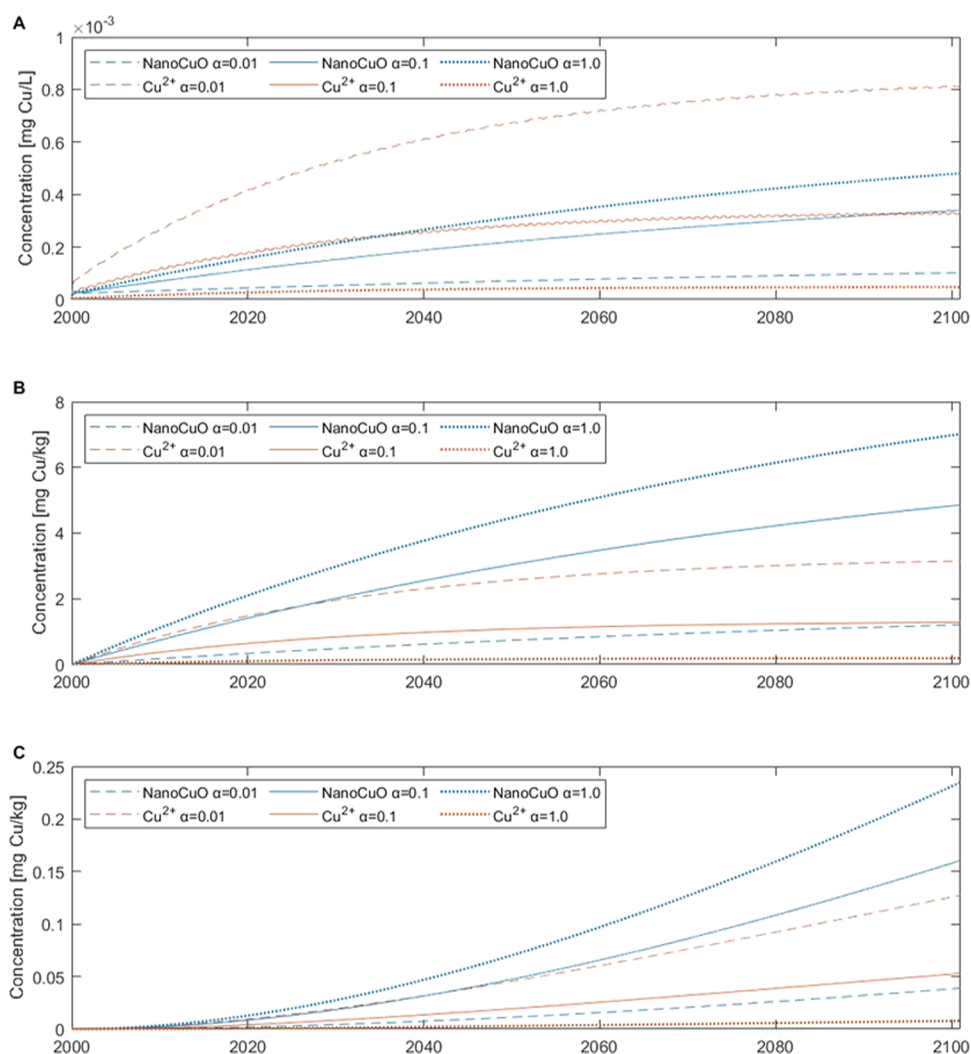


Figure 4. Accumulation of nanoCuO and Cu²⁺ in the water column ((A) water column and sediments (B) surface sediments and (C) subsurface sediments) of Lake Waccamaw in our $\alpha = 0.01$ case (dashed lines), $\alpha = 0.1$ case (lines), and $\alpha = 1.0$ case (dotted lines) between January 1, 2000 and January 1, 2101.

positive charge have an attachment efficiency of 1, meaning that they heteroaggregate completely. The charge of nanoCuO has been found to vary in aquatic environments based on various factors, including water pH and ligand profile,^{29,64,65} which suggests that our usage of an attachment efficiency of 0.1 may underestimate the heteroaggregation and subsequent sedimentation/accumulation of nanoCuO.

Increased buildup of nanoCuO may have serious implications on benthic and pelagic organisms. Copper-based ENMs have been found to be toxic to organisms such as fish, crustaceans, algae, and bacteria at concentrations as low as 0.04 to 0.06 mg/L.⁶⁶ Furthermore, toxicity thresholds of Cu²⁺ have been found to vary among aquatic species, ranging from as low as 5.0×10^{-3} mg/L to as high as 64 mg/L.¹³ Our study showed that simulated concentrations of nanoCuO and Cu²⁺ are below toxicity levels in the water column of Lake Waccamaw, but this could change if the number of boats moored increased, and thus the loading rate of nanoCuO-based antifouling paints were to increase (as evidenced through the linear response of our model when we simulated changes in loading rate; Figure S3). Additional research targeting copper toxicity in the sediments, which varies based on sediment/system properties, would help researchers better

compare results to established toxicity thresholds. This would be particularly helpful in our system, which showed a tendency for both nanoCuO and Cu²⁺ accumulation in the sediments.

3.2. Downstream Release of Copper. We estimate that the mass load of total copper (nanoCuO and Cu²⁺) leaving Lake Waccamaw each day via advection reaches 151 g Cu/day after 101 years. This load consists of an approximately even distribution of nanoCuO and Cu²⁺ (Figure S5). Our results highlight the importance of considering and/or monitoring downstream implications of ENM additions. It is important to note that our model assesses the accumulation of nanoCuO and Cu²⁺ specifically for the Lake Waccamaw system, based on estimated nanoCuO loading rates from 337 boats. The mass copper load may increase if the population around Lake Waccamaw, and subsequently, the number of boats permanently moored in the lake, increase.

3.3. System Response after the Removal of NanoCuO Load. To simulate a recovery period for Lake Waccamaw, we removed the nanoCuO source after 50 years of loading (Figure 3). Even after an additional 51 years with no nanoCuO inputs, nanoCuO and Cu²⁺ concentrations did not reach zero in the water column or sediment layers. Once the nanoCuO source is removed, we saw a sharp drop in both nanoCuO and Cu²⁺

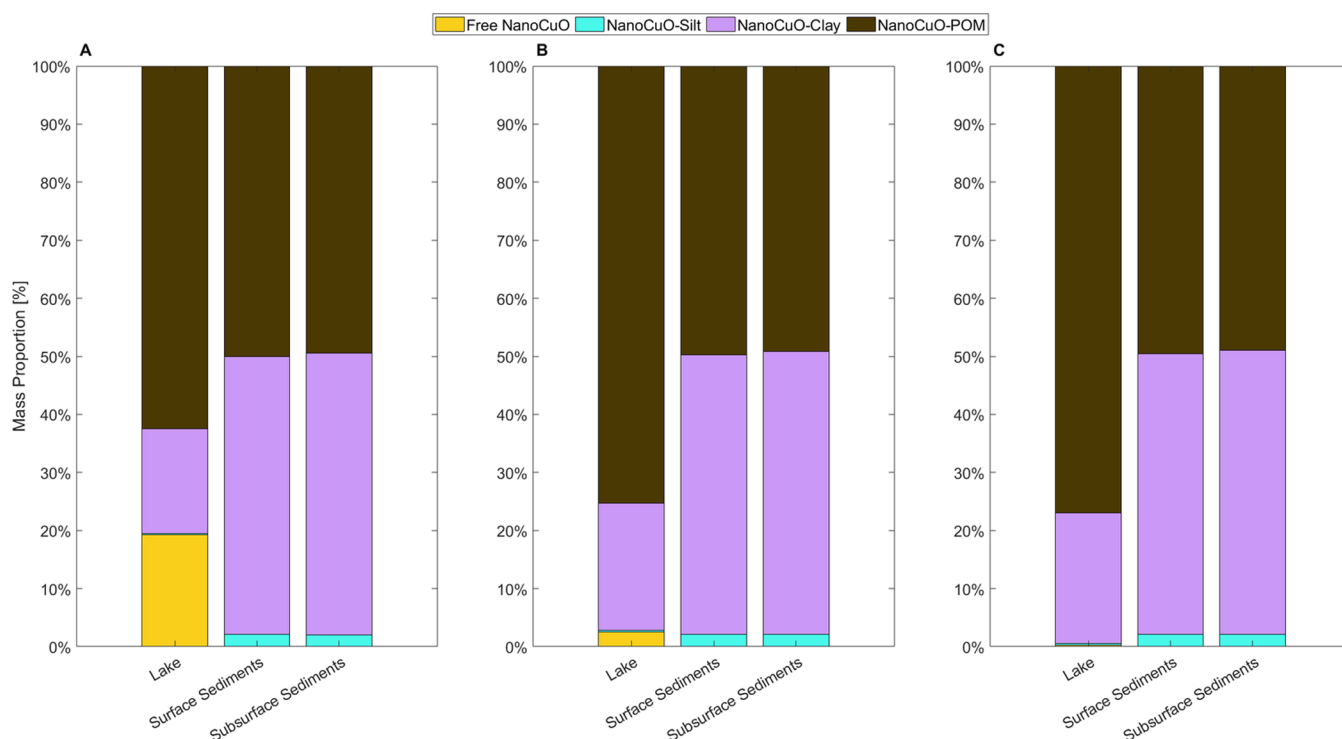


Figure 5. Mass proportion of each form of nanoCuO (free and heteroaggregated nanoCuO) relative to the total mass of nanoCuO in each compartment in our (A) $\alpha = 0.01$ case, (B) $\alpha = 0.1$ case, and (C) $\alpha = 1.0$ case.

concentrations in the water column, which represents materials lost from the system via outflow. Concentrations decreased over time in the water column and surface sediments but were not completely eliminated after 51 years. Both nanoCuO and Cu^{2+} concentrations continued to increase over time in the subsurface sediments, although the rate of increase slowed once the ENM load was removed (Figure 3). In the water column, surface sediments, and subsurface sediments, nanoCuO concentrations were higher than Cu^{2+} concentrations after the 51-year recovery period. Our simulations suggest a strong persistence of contamination in Lake Waccamaw for both the water column and sediments, likely due to competing processes of settling and diffusion/resuspension, even if the use of nanocopper-based boat-bottom paints were eliminated.

3.4. Model Variations as a Function of Attachment Efficiency. **3.4.1. Accumulation and Mass Proportions of NanoCuO and Cu^{2+} .** To investigate how the fate and transport of nanoCuO and Cu^{2+} vary as a function of attachment efficiency (α_{het}), we compared our $\alpha = 0.01$ case and $\alpha = 1.0$ case results to our $\alpha = 0.1$ case results. Figure 4 shows the concentrations of total nanoCuO (including free nanoCuO and nanoCuO aggregates) and Cu^{2+} (free, complexed, and sorbed Cu^{2+}) between January 1, 2000 and January 1, 2101 in our three model compartments. Our $\alpha = 0.01$ case showed a more gradual increase in nanoCuO concentration and a faster increase in Cu^{2+} concentration in the water column and sediments, ultimately yielding lower nanoCuO and higher Cu^{2+} concentrations than in our $\alpha = 0.1$ case (Figure 4A). Our $\alpha = 1.0$ case yielded opposite results; in the water column, surface sediments, and subsurface sediments, nanoCuO accumulated at a faster rate to reach a higher concentration after 101 years than reported in our $\alpha = 0.1$ case, while Cu^{2+} concentrations increased more slowly and reached a lower concentration than in our $\alpha = 0.1$ case (Figure 4C).

Our results highlight the influence that α_{het} has on the speciation of nanoCuO inputs. Unsurprisingly, our model suggests that high α_{het} favors rapid heteroaggregation of nanoCuO, and thus is more likely to maintain its nanomaterial form rather than dissolving to yield Cu^{2+} . Subsequently, when we evaluated the mass proportions of nanoCuO and Cu^{2+} present in each $\alpha = 1.0$ case compartment, we found that the total copper was composed of 91% nanoCuO in the water column and 97% in both the surface and subsurface sediments. Praetorius et al.⁶ assessed the influence that a range of attachment efficiencies ($\alpha_{\text{het}} = 0.001, 0.01, 0.1, \text{ and } 1.0$) has on the accumulation of titanium oxide (TiO_2) nanoparticles in a river. Increased α_{het} favored heteroaggregation, which boosted the removal of free TiO_2 nanoparticles from the water column and increased concentrations of particulate matter-bound TiO_2 nanoparticles. As high α_{het} increases concentrations of aggregates in Lake Waccamaw, it may also increase the resuspension of these aggregates back into the water column after sedimentation, which may be why we did not see a pronounced drop-off of nanoCuO in the water column as aggregates settled into the sediments. The heightened accumulation of Cu^{2+} in our $\alpha = 0.01$ case suggests that low α_{het} increases the amount of time it takes for nanoCuO to aggregate with suspended particulate matter (SPM), thus allowing more nanoCuO dissolution. This increased time may have resulted in the large proportion of Cu^{2+} we found in all compartments of our $\alpha = 0.01$ case; copper was found primarily in the form of Cu^{2+} in the water column and sediments, making up 89% of total copper in the water column, 72% in the surface sediments, and 77% in the subsurface sediments.

Although accumulation varied seasonally in the water column in all of our simulations, the magnitude of the variation differed among attachment efficiencies (Figure 4).

We detected the largest seasonal variations in Cu^{2+} in our $\alpha = 0.1$ case, followed by our $\alpha = 0.01$ case, and finally our $\alpha = 1.0$ case. The impact of seasonality appears to vary less among attachment efficiencies for nanoCuO accumulation. Our results are consistent with the bulk concentration results, suggesting that at a high α_{het} , nanoCuO aggregates quickly with solid particles, meaning that it remains a nanomaterial rather than dissolving to yield Cu^{2+} . Our results also suggest that competing governing process appears to control the impact of seasonality, particularly on Cu^{2+} accumulation.

3.4.2. Mass Proportions of Free NanoCuO and NanoCuO Aggregates. To further assess attachment efficiency's impact on the behavior of nanoCuO in Lake Waccamaw, we quantified the mass proportions of each form of nanoCuO present in the compartments of our $\alpha = 0.01$, 0.1, and 1.0 cases (Figure 5). Specifically, we investigated how the ratio of free nanoCuO, nanoCuO-silt, nanoCuO-clay, and nanoCuO-POM varies based on α_{het} in the water column, surface sediments, and subsurface sediments. Notably, the proportion of free nanoCuO in the water column differed among attachment efficiencies. As α_{het} increased, the proportion of free nanoCuO in the water column decreased. The highest water column free nanoCuO proportion was seen in the $\alpha = 0.01$ case (19%; Figure 5A), followed by the $\alpha = 0.1$ case (2.5%; Figure 5B), and finally the $\alpha = 1.0$ case (0.27%; Figure 5C). This trend is unsurprising; as α_{het} increases, free-floating nanoCuO particles aggregate with SPM more quickly in the water column.

In our simulations, POM and clay particles formed the largest proportion of nanoCuO aggregates, followed by silt particles (Figure 5). This highlights the importance that the distribution of fine inorganic and organic particles has on nanoCuO dynamics, a phenomenon which has been reported by other studies targeting heteroaggregation of nanoCuO^{17,30} and other ENMs.^{26,40,67}

In addition to α_{het} and collision frequency, the heteroaggregation rate of a nanomaterial is also driven by the number of suspended particles available for aggregate formation (eq S3). In our model, water column concentrations of POM were higher than all other solids, followed by clay (~50% of POM concentrations) and then silt (an order of magnitude less than POM concentrations; Table S3). Other than nanoCuO, POM and clay are the smallest particles included in our simulations. When comparing equal concentrations of particles, a decrease in particle size leads to an increase in the amount of surface area available for interactions.⁶⁸ Furthermore, because POM and clay particles sediment out of the water column at a slower rate than silt particles, they likely have more time to aggregate with nanoCuO than the amount of time available for silt particles. The combined effect of the increased number of particles, time spent in the water column, and surface area of POM and clay particles likely contributed to the larger proportion of aggregate formation with nanoCuO.

4. CONCLUSIONS

Metallic ENMs dissolve to yield metal ions, which are conserved in environmental systems. This is particularly concerning when the metal ions produced are toxic, as is the case for nanoCuO. Our simulations suggest that as nano-copper-based antifouling paints are loaded into Lake Waccamaw, most accumulation of nanoCuO and Cu^{2+} takes place in the sediments due to particle attachment through sorption and heteroaggregation. While Cu^{2+} accumulation slowed in the water column and surface sediments, nanoCuO

concentration continuously increased in the water column, surface sediments, and subsurface sediments for 101 years for all attachment efficiencies we investigated. Although sediment accumulation removes a portion of nanoCuO and Cu^{2+} from the water column, this removal may not be permanent; shifts in water quality may lead to remobilization of Cu^{2+} , and resuspension could transfer both copper species back into the water column. Thus, accumulation may threaten the well-being of both pelagic and benthic organisms, a threat which could increase in severity if the number of boats and/or usage of nanocopper-based antifouling paints on boats in Lake Waccamaw increase.

NanoCuO and Cu^{2+} accumulation in the water column was influenced by temperature, which suggests that their behavior could be impacted by climate change. Attachment efficiency largely influenced the speciation of nanocopper inputs. High α_{het} causes rapid heteroaggregation of nanoCuO with SPM, allowing less time for the dissolution of nanoCuO to Cu^{2+} , while the opposite trend is evident at low α_{het} .

Although we used WASP8 to create a model specific to Lake Waccamaw, a similar approach could be used to simulate nanocopper loading in other freshwater environments. Researchers could also easily use this model to examine ENM behavior in lakes with characteristics similar to those of Lake Waccamaw, namely, well-mixed freshwater lakes.

Future research targeting the specific attachment efficiency associated with nanoCuO in various aquatic systems, as well as climate change's potential impact on nanoCuO accumulation, mass loading, and environmental exposure risks, may prove beneficial. WASP8 serves as a powerful tool for modeling the environmental fate and transport of ENMs and providing insight into the regulatory and toxicological implications of using ENM-based products.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.2c00157>.

Additional information on model parameterization, calculations, seasonal variation of copper species, and mass copper load (PDF)

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Funding

This work was funded by the U.S. Environmental Protection Agency's Chemical Safety for Sustainability program in the Office of Research and Development (CSS 3.1.6: Emerging Contaminants; Model Fate and Transport of Nanomaterials in Surface Waters).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported in part by an appointment to the ORISE participant research program, an interagency agreement between the U.S. Environmental Protection Agency and the Department of Education, and the U.S. Environmental Protection Agency's Chemical Safety for Sustainability program. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and has been approved for publication (ORD-046382). Mention of trade names or commercial products does not constitute an endorsement or recommendation for use. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

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