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New Perspectives on Nanomaterial Aquatic Ecotoxicity: Production Impacts Exceed Direct Exposure Impacts for Carbon Nanotubes

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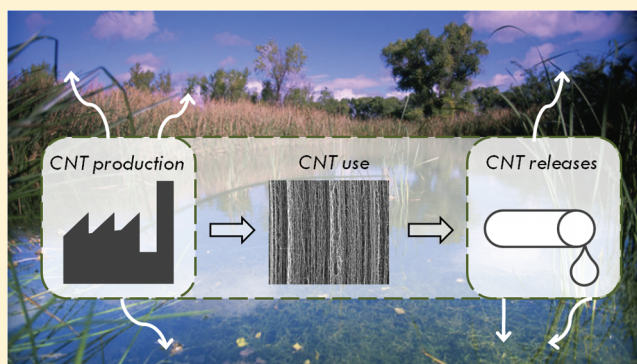
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S Supporting Information

ABSTRACT: Environmental impacts due to engineered nanomaterials arise both from releases of the nanomaterials themselves as well as from their synthesis. In this work, we employ the USEtox model to quantify and compare aquatic ecotoxicity impacts over the life cycle of carbon nanotubes (CNTs). USEtox is an integrated multimedia fate, transport, and toxicity model covering large classes of organic and inorganic substances. This work evaluates the impacts of non-CNT emissions from three methods of synthesis (arc ablation, CVD, and HiPco), and compares these to the modeled ecotoxicity of CNTs released to the environment. Parameters for evaluating CNT ecotoxicity are bounded by a highly conservative “worst case” scenario and a “realistic” scenario that draws from existing literature on CNT fate, transport, and ecotoxicity. The results indicate that the ecotoxicity impacts of nanomaterial production processes are roughly equivalent to the ecotoxicity of CNT releases under the unrealistic worst case scenario, while exceeding the results of the realistic scenario by 3 orders of magnitude. Ecotoxicity from production processes is dominated by emissions of metals from electricity generation. Uncertainty exists for both production and release stages, and is modeled using a combination of Monte Carlo simulation and scenario analysis. The results of this analysis underscore the contributions of existing work on CNT fate and transport, as well as the importance of life cycle considerations in allocating time and resources toward research on mitigating the impacts of novel materials.



INTRODUCTION

Characterizing exposure to nanomaterials, via release and transport, is fundamental to understanding their environmental risk. Release studies estimate that environmental discharge of manufactured nanomaterials will occur primarily through emissions to wastewater treatment facilities, landfills, and soils.¹ Some portion of these emissions are expected to make their way into aquatic ecosystems, though the extent of nanomaterial migration will depend heavily on physicochemical interactions with surrounding environmental media,^{2–4} environmental and biological transformations of the nanomaterials,^{5,6} and environmental management policies established to reduce risk.^{7–9}

Once discharged to the environment, nanomaterials will interact with biological systems. In the case of carbonaceous nanomaterials such as carbon nanotubes (CNTs), any toxicity that results from these interactions will depend on physicochemical and electronic properties, including nanotube purity (residual metal and amorphous carbon content), diameter, length, surface charge, functionalization, chirality, and aggregation state.¹⁰ Nanomaterial toxicity is also correlated

to the aquatic chemistry of the suspending solution, especially as it affects the physicochemical properties of the nanomaterials. For example, the reduced toxicity of nanomaterials in high ionic strength solutions is most likely attributable to the increased aggregation of carbonaceous nanomaterials in saline environments.¹¹

The mechanistic relationship between nanomaterial properties and toxicity has been probed through single-cell, in vitro experiments on bacteria,^{12,13} algae,^{14,15} protozoa,¹⁶ epithelial,¹⁷ fibroblast cells,¹⁸ and human blood serum.¹⁹ Extrapolation of this property-dependent relationship to toxicity in multicellular organisms has also been attempted, though the results are sometimes difficult to interpret. At higher trophic levels, toxicity exhibits strong dependence on uptake pathways, biotransformation, distribution, and removal of nanomaterials through physiological mechanisms specific to the organism.

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Comprehensive nanotoxicity assessment in aquatic organisms is further complicated by the potential for toxicity on different time scales measured through acute, chronic, and bioaccumulation testing. A collection of studies has addressed varying toxicity pathways in aquatic organisms, including an assortment of copepods,^{20–22} *Daphnia magna*,^{14,22–28} hydra,¹⁴ amphibian larvae,²⁹ zebrafish,^{30–32} and trout.³³ Standardization of ecotoxicity analysis methods and expanding insight into nanomaterial environmental behavior is driving additional research in this area, but there is still widespread uncertainty about the quality of existing data and its relevance in environmental systems.

Balancing this end-of-life research on nanomaterial toxicity is a smaller literature on the environmental impacts of producing nanomaterials. These studies have considered several categories of environmental impacts, including materials and energy use, greenhouse gas emissions, and toxicity. On a mass basis, the *E*-factor, or the total quantity of materials needed to produce and purify various nanomaterials relative to the masses produced, was estimated at 100–100 000, larger than that for pharmaceuticals or fine chemicals.³⁴ Several studies have considered life cycle energy use for carbon nanofibers,³⁵ fullerenes,³⁶ single-walled carbon nanotubes (SWNTs), and multiwalled carbon nanotubes (MWNTs)^{36–38} across a variety of production methods, finding that carbonaceous nanomaterials require 2–100 times as much energy to produce as primary aluminum, a benchmark energy-intensive metal. Nonenergy considerations have been discussed by Plata et al., who presented a mass inventory of side products and emissions from SWNT production to air and water.³⁹ More qualitatively, Sengul et al. reviewed various nanomanufacturing methods and highlighted key processes in terms of chemical inputs of concern, high energy consumption, and the creation of processing waste,⁴⁰ and Robichaud et al. performed a relative risk analysis that compared fabrication risks of several nanomaterials to those of common industrial products.⁴¹ Few studies have quantitatively considered a broad range of environmental impacts. One exception is Healy et al.,³⁸ who conducted a life cycle assessment (LCA) of SWNT production using three synthesis techniques examining releases of carcinogens, airborne inorganics, greenhouse gases, and acidifying substances, as well as use of energy and mineral resources.

The common feature of each of the production-focused LCA studies is that they are all cradle-to-gate studies, and so do not consider the impacts of nanomaterial release during product use or end-of-life disposal. For this reason, the toxicity of the CNTs themselves has not been considered in any LCA studies to date, in part because this information is not readily available in current LCA databases or impact assessment methods. Robust estimates of CNT releases from specific products under a variety of physical and environmental conditions are also sparse. Conversely, the growing body of literature on CNT environmental fate and transport has largely focused on releases of nanomaterials, while omitting production-side impacts.⁴² This issue has recently been recognized as a substantial impediment to a systemic understanding of the environmental implications of nanomaterials, and several recent articles have called for research that integrates all stages of the life cycle.^{43–45}

In this study we develop a life cycle framework for evaluating the ecotoxicity of carbonaceous nanomaterials across several life cycle stages. Our goal is to compare the relative impacts of CNT production and exposure using a shared metric of aquatic

ecotoxicity. The present study utilizes existing life cycle inventory data for three methods of CNT production and combines toxicological studies with the recent consensus USEtox impact assessment model to determine appropriate bounds on the ecotoxicity of CNTs released to the environment. By integrating these two areas of research into a comprehensive life cycle study, we show the relative importance of each stage to total environmental impacts and highlight future areas of beneficial research.

METHODS

The life cycle ecotoxicity of CNTs was assessed in three steps: (i) building the life cycle inventory (LCI) for material and energy inputs and emissions from CNT production processes, (ii) building the ecotoxicity characterization factor for CNTs at their point of release into the environment, and (iii) using an integrated fate, transport, and toxicity model to perform ecotoxicity impact assessment for the emissions tabulated in (i) and (ii).

Life Cycle Inventory of CNT Production. Data on the material and energy inputs and emissions associated with CNT production were gathered from Healy et al.³⁸ This data set covers production by the three most common methods of CNT synthesis: arc ablation, chemical vapor deposition (CVD), and high-pressure carbon monoxide (HiPco). Synthesis reaction yields for the various processes were assumed to be 4.5%, 3.0%, and 0.1%, respectively, and purification yields at 70% for arc ablation and 90% for CVD and HiPco processes.³⁸ A reference flow of 1 kg of CNTs was used as the basis of comparison among synthesis techniques. The scope includes the raw material inputs and emissions from production of all reagents and ancillary materials, as well as the extraction, conversion, and delivery of energy inputs. CNT production was considered from catalyst preparation through synthesis, purification, inspection, and packaging processes. Purification and washing were carried out mainly with deionized water and nitric acid, which were assumed not to be recovered. Excluded from the analysis were the production equipment, facilities, and control systems (e.g., HVAC and air filtration) of the manufacturing site. Data were input into SimaPro 7.3 LCA software, which then generated a mass inventory of 262 discrete chemical emissions to air, 209 emissions to water, and 57 emissions to soils.

Development of CNT Ecotoxicity Characterization Factors. Life cycle impact assessment methods describe environmental impacts in terms of characterization factors. For toxicity impacts, these factors depend on the inherent toxicity of the substance, as well as information on fate and transport and potential routes of exposure. The present work makes use of the recent USEtox model⁴⁶ (www.usetox.org) that incorporates these parameters into a single framework for estimating the characterization factors (*CF*) of a substance:

$$CF = EF \cdot FF \cdot XF \quad (1)$$

where *EF* is the effect factor, *FF* is the fate factor, and *XF* is the exposure factor.⁴⁶ The development of each factor is discussed below. The characterization factor *CF* for each scenario was then calculated, with units describing the temporal and volumetrically integrated potentially affected fraction of aquatic organisms per unit mass of CNTs released (PAF m³ day kg^{−1}). USEtox defines this as Comparative Toxic Units for Ecosystems (CTU_e).⁴⁶

Table 1. Past Studies of CNT Aquatic Toxicity for Selected Organisms

type	genus species	test type	test details	EC50 (mg/L)	ref
bacteria	<i>E.coli</i> , <i>P. aeruginosa</i> , <i>S. aureus</i> , <i>B.subtilis</i>	membrane integrity	reported as 5–100 mg/L	5	49
protozoa	<i>Stylonychia mytilus</i>	uptake and growth inhibition		1	16
algae	<i>Pseudokircheriella subcapita</i>	growth inhibition	sublethal, IC-25 value	1	14
copepods	<i>Amphiascus tenuiremis</i>	mortality	concentration of 10 mg/L gives 35% mortality for unpurified SWNT; 20% for purified	5	20
	<i>Amphiascus tenuiremis</i>	fertilization/molting	concentration of 1 mg/L gives No Observed Effect for purified SWNT	9	20
daphnia	<i>Daphnia magna</i>	LC50	reported as 2.4–15 mg/L	1.2	26–28
hydra	<i>Hydra attenuata</i>	sublethal morphological change	reported as 1–10 mg/L	1	14
fish	<i>Oncorhynchus mykiss</i>	respiratory toxicant	reported as 0.1–0.5 mg/L	0.1	33
	<i>Danio rerio</i>	hatching delay	240 mg/L for MWNT	120	30

Effect Factor. First, the ecotoxicological effect factor EF of CNTs was estimated from reported CNT toxicity toward freshwater aquatic organisms. In USEtox, the EF reflects the relationship between the potentially affected fraction (PAF) of aquatic organisms and the concentration of a pollutant. Specifically, it is defined as the slope of the concentration–response relationship up to the point when the PAF reaches 50%:

$$EF = \frac{PAF}{HC50} = \frac{0.5}{HC50} \quad (2)$$

where $HC50$ is the geometric mean of species-specific $EC50$ data, and $EC50$ is the effective concentration of a pollutant at which 50% of a single species population experiences a response. Therefore, the $HC50$ refers to the hazardous concentration at which 50% of the species are exposed above $EC50$ levels. Assuming a log-normal distribution of species sensitivity, the geometric mean provides an estimate of central tendency that is less affected by extreme values than geometric or harmonic means of $EC50$ toxicity data.

The present study aims to be as conservative as possible in estimating the ecotoxicity of CNTs in aquatic ecosystems. The body of research describing CNT toxicity is growing rapidly but is still small, covering relatively few species and with little corroboration of results. Table 1 gives a summary of aquatic toxicity tests for CNTs to date. Among similar species, there is significant variation in the toxicological end points considered, spanning acute factors (mortality) and chronic factors (growth or reproductive inhibition, changes in morphology). The reports are also inconsistent in the type of CNTs used as toxicants, in some cases relying on uncharacterized CNTs. The large variation in physicochemical properties and associated toxicities of CNTs as a class of materials is a major impediment to making robust estimates of their ecotoxicity. Given the limitations of data availability, we make no distinction between single-walled and multiwalled nanotubes, the purity of the nanotube sample, or other physicochemical properties that differ between experimental designs. The implications of this assumption are considered in the Results and Discussion section.

Given the multiple differences among the sample studies and the lack of standard testing and characterization procedures for CNTs, several model assumptions were made that aim to err on the side of overestimating aquatic impacts. First, the lowest reported $EC50$ or $LC50$ (lethal concentration) for each species was used to calculate the $HC50$, although USEtox suggests a

less conservative estimate that averages the toxicity data from each species, followed by an average for each genus.⁴⁶ The USEtox model guidelines prioritize studies that report chronic toxicity values when quantifying environmental impact, and where chronic data are unavailable, the guidelines suggest an acute-to-chronic ratio (ACR) of 2.⁴⁷ Where a no observed effect concentration (NOEC) was reported, we extrapolated from this NOEC to an $EC50$ using a factor of 9, as recommended by USEtox based on previous statistical correlations for noncancer end points.⁴⁸

Additionally, response levels for many nanomaterials were reported for arbitrary CNT concentrations selected during experimental design (often the solubility limit of CNTs in aqueous solution), rather than for the conventional concentration of CNTs at the $EC50$ or $LC50$ point. This forced a decision about whether to extrapolate the CNT concentration out to the 50% effect level or to use the highest concentration tested, which was often associated with an upper toxicity limit closer to 20% or 30%. Following a conservative approach, the highest concentration of CNT tested was used as the $LC50$ or $EC50$ value. This conservative approach is amplified by the fact that toxicity tests were rarely conducted with purified nanotubes, and there may be increased mortality or chronic impacts from residual metal or solvent impurities, thus overestimating the toxicity of the CNTs themselves.

Fate Factor. Next, the multimedia fate and transport module of the USEtox model was utilized to determine the fate factor FF of CNTs released into the freshwater environment. FF is the residence time of a substance in a particular environmental compartment (such as urban air), with units of days. USEtox uses physicochemical properties of substances as input parameters to model transport among different phases as well as loss rates. Losses can occur through adsorption to suspended solids and subsequent sedimentation, volatilization, degradation, and advection.⁵⁰ Aggregation and settling represents another loss pathway for CNTs.⁵¹ Although this important colloidal mechanism is not directly accounted for by the USEtox model, it was accounted for exogenously.

The present study models two scenarios for CNT toxicity, with the parameter values for each scenario detailed in Table 2. An unrealistic “worst case” scenario was developed using highly conservative parameter values that maximize exposure of aquatic organisms to CNTs. First, we assume that 100% of produced CNTs will be released directly to the water column. Next, we maximized interaction between the aquatic organisms and suspended CNTs. This was accomplished by assuming

Table 2. CNT Fate and Transport Parameters for LCA Scenarios

parameter	unit	worst case	realistic	ref
fraction of CNTs released to environment		1.0	0.002	1,42
molecular weight ^a	g mol ⁻¹	1 × 10 ⁵	1 × 10 ⁵	53
octanol–water partition coeff. K_{OW}		1 × 10 ⁵	1 × 10 ⁰	21,54
organic carbon–water partition coeff. K_{OC}	L kg ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁷	55
Henry's law coeff. 25 °C, K_H	Pa kg mol ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁻²⁰	46
solubility in deionized water (25 °C)	mg L ⁻¹	2 × 10 ⁴	1 × 10 ¹	56,57
dissolved carbon–water partition coeff., K_{DOC}	L kg ⁻¹	1 × 10 ⁻²⁰	1 × 10 ³	52
suspended solids–water partition coeff., K_{pSS}	L kg ⁻¹	1 × 10 ⁻²⁰	1 × 10 ³	52
sediment–water partition coeff., K_{pSd}	L kg ⁻¹	1 × 10 ⁻²⁰	1 × 10 ³	52
soil–water partitioning coeff., K_{pSl}	L kg ⁻¹	1 × 10 ⁻²⁰	1 × 10 ³	52
aggregation and settling	%	0	90	42
degradation rate in air	s ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁻²⁰	6
degradation rate in water	s ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁻²⁰	6
degradation rate in sediment	s ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁻²⁰	6
degradation rate in soil	s ⁻¹	1 × 10 ⁻²⁰	1 × 10 ⁻²⁰	6
bioaccumulation factor in fish/biota, BAF_{fish}	L kg ⁻¹	5 × 10 ³	5 × 10 ⁻²	46,58

^aBased on a density of 1.3 g cm⁻³ and a length of 100 nm.

partitioning coefficients that strongly favor the water column over dissolved organic carbon, suspended solids, sediments, or soils; extreme hydrophobicity leading to high rates of bioaccumulation; no aggregation; and no degradation or other losses. This is an unrealistic scenario as any hydrophobic substance will tend to partition out of the water column, but represents the worst possible model result in order to give an absolute upper bound on CNT ecotoxicity in the model.

The second scenario is a realistic estimate using values derived from the general literature. Currently, most CNTs in consumer products are bound to polymer matrices or contained by the casings of electronics. The most robust estimates of the fraction of CNTs entering commerce that are eventually released to surface water bodies give values between 0.1 and 0.3% of the total.^{1,42} This factor by itself reduces the potential ecotoxicity of CNTs by 3 orders of magnitude from the worst case scenario. CNTs in the water column will partition preferentially to dissolved organic carbon, as CNTs have been shown to be powerful adsorbents of organic compounds.¹¹ In a theoretical study of manufactured carbon-based nanoparticle sedimentation, Koelmans et al. estimate a sediment–water partitioning coefficient K_{pSd} of 10³ L kg⁻¹, which was also applied here to the suspended solids and soils phases.⁵² Following Gottschalk et al., the fraction of CNTs lost from the water column due to aggregation and settling of CNTs was estimated at 90%.⁴² Though there have been reports of biodegradation of CNTs under laboratory conditions,⁶ we have assumed here negligible degradation rates for CNTs in all environmental media.

The colloidal nature of CNTs complicates the estimation of realistic values that are appropriate given the dissolved chemical fate and transport model employed in USEtox. For example, fullerenes have been shown to resist crossing the water–octanol

boundary layer in either direction,²¹ rendering the K_{ow} parameter inapplicable. This and related modeling difficulties are addressed in the Discussion section below.

Exposure Factor. The final component of the characterization factor for CNT ecotoxicity is the exposure factor (XF), which USEtox defines for freshwater ecotoxicity as the dissolved fraction of CNTs in the water column, determined by

$$XF = 1 / \left(1 + \left(K_{pSS} \cdot SS + K_{DOC} \cdot DOC + BAF \cdot BIOMass \right) \cdot 10^{-6} \right) \quad (3)$$

where SS, DOC, and BIOMass are the assumed concentrations in freshwaters of suspended solids (15 mg L⁻¹), dissolved organic carbon (5 mg L⁻¹), and biota (1 mg L⁻¹), respectively.⁴⁶

Ecotoxicity Impact Assessment. The USEtox model was published with a large set of precalculated recommended CFs for organic chemicals and a draft set of factors for inorganic substances for emissions to air, water, and soils. The life cycle inventory associated with CNT production described above was matched by CAS number with these two sets of CFs and the row products were summed to determine the total ecotoxicity of all emissions associated with CNT production using each of the three synthesis methods, based on a consistent production flow of one gram of material. The ecotoxicity resulting from one gram of CNT synthesis was then compared to the ecotoxicity of the relative proportion of that one gram of CNTs that is released to the environment during product use and disposal. Losses of CNTs to the environment during their production or incorporation into products, while not explicitly considered here, could easily be incorporated in the release fraction parameter.

Uncertainty. There exists significant uncertainty in the estimates of production and release-based ecotoxicities, related both to the models employed and to the values assumed for the input parameters. Uncertainty was assessed separately for each stage of the CNT life cycle. The material and energy inputs, outputs, and reaction yields are based on lab-scale experiments from 2007. Actual industrial practices are expected to be much more energy- and material-efficient, both currently and in potential future scale-up. To capture these likely efficiencies, a scenario was constructed that assumes complete recycling of purification agents such as nitric acid, and an increase in CNT yields to 10% from the assumed levels of 4.5% and 3% for arc and CVD methods, respectively. HiPco yields are assumed to increase from 0.1% to 1%. Uncertainty arising from the USEtox model is difficult to estimate across the hundreds of substances that arise from CNT production; however, the developers of USEtox specifically caution about the results for metals, as these CFs are currently considered interim values. The CFs for all metals were thus varied by an order of magnitude in each direction to capture model uncertainty for all scenarios. For CNT release-based ecotoxicity, a Monte Carlo analysis was performed within the USEtox model. Each input parameter was assigned a uniform distribution from which values for each model run were randomly sampled. The ranges assumed were 0.1–1% for the release fraction, 80–99% for the CNT fraction lost to aggregation and settling, and plus or minus an order of magnitude for all other parameters from the values given in Table 2, as well as for the HCS0 effect factor.

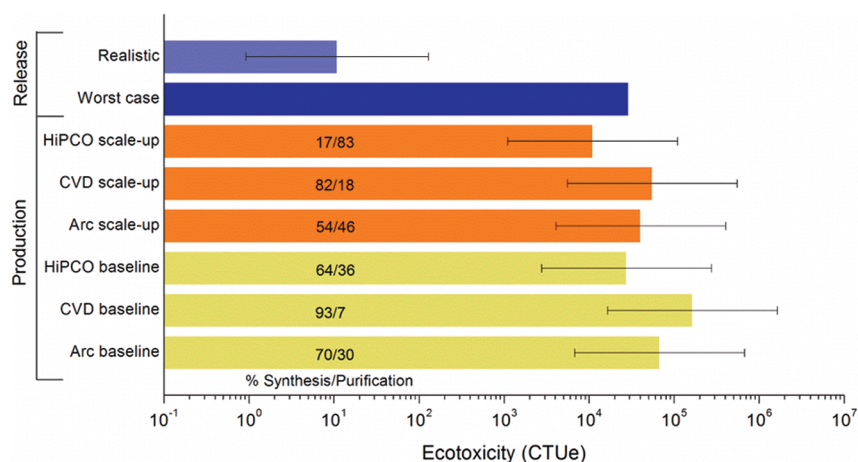


Figure 1. Ecotoxicity impacts from direct release and production scenarios, in CTUe ($\text{PAF m}^3 \text{ day}$).⁴⁶

RESULTS AND DISCUSSION

Comparative Ecotoxicity Impacts. The first set of USEtox model outputs are the three components *EF*, *XF*, and *FF* (eq 1) of the characterization factor for CNTs under the conservative assumptions for each of the worst case and realistic scenarios. The *EF*, as an inherent measure of ecotoxicity, is the same for both scenarios, under the simplifying assumption that there are no physical differences between CNTs in the two scenarios, such as functionalization, that might affect their fundamental toxicity. This assumption is explored in greater detail below. The *HC50* for CNTs based on the results in Table 1 had an estimated mean value of 2.5 mg L^{-1} , resulting in a freshwater ecotoxicity *EF* of $200 \text{ PAF m}^3 \text{ kg}^{-1}$, and was varied between 0.25 and 25 mg L^{-1} in the Monte Carlo analysis.

While the *EF* remains constant between the two scenarios, both the *FF* and the *XF* vary depending on the input parameters in Table 2. In the conservative scenario, the *FF* gives a CNT residence time of 143 days. Under this set of model parameters, there is no degradation and the only loss of CNTs from the freshwater compartment of the multimedia model is by advection into oceans. The *XF* for the worst case scenario predicts that 100% of CNTs in the water column have the potential for exposure to aquatic organisms. These are both expected results and validate the model parameters chosen in Table 2. Combining the three components in eq 1 gives a conservative characterization factor of $29\,000 \text{ PAF m}^3 \text{ day kg}^{-1}$. This is a measure of ecotoxicity impact per kg of CNTs released. As we are assuming that all of the CNTs produced in this scenario are released to the environment, the upper bound worst case potential impact of CNTs is therefore estimated at $29\,000 \text{ PAF m}^3 \text{ day}$.

For the realistic scenario where Monte Carlo analysis was employed, the mean residence time is calculated to be on the order of days, with the decrease from the conservative case largely attributable to aggregation and subsequent settling and adsorption to soils and sediments. The CNT exposure factor *XF* in the water column is 98%, with the majority of the remaining 2% partitioning to suspended solids in the model. The assumed concentration of solids in freshwaters is 15 mg L^{-1} ; increasing this endogenous model parameter would decrease the exposure factor *XF*. Again using eq 1, the mean characterization factor in this realistic scenario is $3700 \text{ PAF m}^3 \text{ day kg}^{-1}$. Multiplying this factor by the environmental release

fraction for CNTs of $0.1\text{--}1 \text{ g CNTs emitted per kg produced}$ over the entire CNT life cycle gives a potential ecotoxicity impact of $11 \text{ PAF m}^3 \text{ day}$. This result is roughly a factor of 2500 less than that of the conservative scenario. Distributions for the Monte Carlo results are shown in Figure S1 of the Supporting Information.

Figure 1 compares the CNT ecotoxicities resulting from the two environmental release scenarios with those resulting from emissions associated with the CNT production scenarios. The analysis reveals that, under the extremely conservative (and highly unrealistic) worst case scenario, ecotoxicity concerns from CNTs released to the environment are equivalent to those from the emissions associated with their production, regardless of the synthesis method employed. However, under realistic assumptions for CNT release fractions, aggregation and settling, partitioning coefficients, and bioaccumulation, the life cycle impacts of CNT production are several orders of magnitude higher than the impacts from their release. Even though there is significant uncertainty in the results both for CNT release and production, there is no overlap in the error bars as shown in Figure 1 for any of the synthesis methods considered. The ecotoxicity impacts associated with CVD production were the largest of all production methods, nearly 2.5 times those of arc ablation, which is in agreement with previous LCA research on nanomanufacturing methods.³⁸ The majority of production impacts are divided between synthesis and purification processes (indicated by the percent splits in Figure 1), but the ratio depends on the production method and skews toward purification in the scale-up scenarios that assume higher synthesis yields.

In this life cycle framework, the emitted substances responsible for causing ecotoxicity may not result directly from CNT synthesis at all, but may instead be only indirectly related, perhaps stemming from the production of reagents or the generation of electricity, for example. The ability to consider the entire techno-economic system is one significant benefit of LCA modeling, allowing users to discern important processes or substances that might be buried in the supply chain or a different product life cycle stage but that drive overall environmental impacts. In this case, the great majority of life cycle ecotoxicity of CNT production results not from unused reagents or direct synthesis products, but indirectly from the emission of bioactive metals, largely from the combustion of fossil fuels for the generation of electricity used during CNT synthesis, or to produce various input chemicals. Detailed

impact assessment results for all substances released for each production method assuming baseline and future production efficiencies are given in Table S1 of the Supporting Information. The most impactful nonmetal emission is phenol, again resulting from upstream combustion processes and from the production of nitric acid, which is used during CNT purification.

Unused reagents and other chemical streams from the various synthesis methods (such as carbon black from arc synthesis) have relatively little impact in this model. This is because their relative quantities are small compared to those associated with upstream energy and material production, and because these wastes are assumed to be strictly managed, either being destroyed via combustion or biodegradation, or sequestered in hazardous waste landfills. Even for the scale-up scenarios that assume higher yields and therefore require less electricity, impacts are still dominated by emissions from the energy sector.

These nonintuitive results suggest that reducing the energy-related emissions associated with CNT synthesis is an important step in reducing their life cycle toxicity. This can be achieved either through supply side measures such as changing the energy mix of power generation or installing more effective pollution control equipment (over which the CNT industry has little control), or through demand-side measures such as improving energy efficiency and yield (over which the industry has direct control). Considering impact categories other than ecotoxicity, Healy et al. modeled both of these scenarios, assuming 100% hydropower electricity and best-achievable synthesis reaction yield improvements, finding order-of-magnitude reductions of impacts in both cases.³⁸ Such life cycle-inspired strategies complement other efforts to characterize and reduce worker exposure to direct synthesis products, or to develop new CNT synthesis methods with few harmful inputs or byproducts. Overall this work quantitatively demonstrates that to minimize the aquatic impacts of CNTs, a three pronged approach should be adopted: (i) improvements of production methods toward greener syntheses, (ii) reduction in CNT exposure by controlling environmental releases, and (iii) improvements to modeling practices for ecotoxicity assessment and transport processes.

Model Application. The present analysis is meant to provide insight into the relative importance of the different life cycle stages of manufactured nanomaterials when considering environmental impacts. While we have estimated several sources of uncertainty here, certain points merit further discussion. First, the USEtox model employed in the current research is recognized for its generalizability to a diverse set of organic and inorganic environmental contaminants. The detailed parameterization of contaminants enables high model integrity across disparate classes of molecules and makes this model useful for predicting the fate and transport of new compounds. However, while the parameters employed in this model describe environmental processes of small molecules, they may not be sufficient for modeling semicolloidal materials like CNTs, which are influenced by both molecular and physical forces. Unlike small molecules whose fate and transport is described by equilibrium partitioning behavior, colloidal behavior is controlled by the kinetics of aggregation, filtration, and deposition. Other physical processes, such as straining and settling, are also unique to colloidal transport models. Colloidal charge, size, and aspect ratio are material properties inherent to the nanoparticle. A range exists for

CNTs, but in general, nanotubes with higher surface charge and larger diameters are more likely to be dominated by kinetics and physical processes. Here, aggregation and settling are represented by a simple partition coefficient, but more detailed kinetic modeling would improve the applicability of the model.

Such kinetic modeling is conceptually difficult for a global model, as colloidal behavior is also strongly dependent on local environmental conditions, including pH, ionic strength, cosolutes, and subsurface matrix characteristics. In general, environmental conditions with low pH, high ionic strength, and low levels of natural organic matter favor nanomaterial aggregation, deposition, and straining. These processes facilitate the incorporation of nanomaterials into soils and sediments, potentially reducing their aqueous concentrations and thus their potential for exposure to aquatic organisms.^{4,51,59} The difficulty of modeling engineered nanomaterials in the environment and the inadequacy of current models has been thoroughly reviewed in a state-of-science report by the U.S. Environmental Protection Agency.⁶⁰

The colloidal nature of CNTs is also important for modeling the effect factor *EF* that reflects CNT toxicity, and may skew standard correlations between concentration and toxicity, and between chronic toxicity and acute toxicity. The present model assumes no difference in the *EF* of CNTs between the conservative and realistic scenarios. Carbon nanotubes are not organics in the conventional sense of being small molecules with toxicity values far below water solubility limits. Under favorable aggregation conditions, high concentrations of CNTs will form large bundles with physicochemical and toxicity characteristics potentially significantly different from their dispersed counterparts, essentially changing the *HC50* of the substance.

The other important challenge to modeling CNT ecotoxicity is in determining appropriate parameter values. While the present analysis is framed in terms of CNTs as a single substance, in reality CNTs represent an entire class of compounds, numbering in the thousands or more. The diversity of physicochemical properties among CNTs complicates the identification of input parameters to the model, as advanced synthesis techniques and functionalization chemistries have made the range of properties enormous. Partitioning, aggregation, and transport parameters are generally only reported for CNTs generally, rather than across a range of diameters, lengths, chirality, and surface functionalization. As for toxicity, there are relatively few studies of aquatic toxicity for *any* CNTs that were appropriate for inclusion in Table 1; gathering a sufficiently large set for assessing a specific nanotube type is not currently possible. We have attempted to bound the uncertainty associated with this parameter uncertainty through Monte Carlo analysis, but a huge gap clearly exists between the current body of research and the number of toxicity studies necessary to make robust, CNT-specific assessments of ecotoxicological risks, to say nothing of risks to human health. This is the greatest barrier to effective and comprehensive assessment (including LCA) of nanomaterials and has significant implications for prioritizing future research as well as for crafting public policy.

Implications. Contemporary environmental research for nanomaterials must develop in two ways. The first is to broaden the lens of toxicity assessment to include life cycle impacts, rather than prioritizing end-of-life, downstream, or direct exposure impacts. The second is to develop predictive

relationships between structure and toxicity that reduce the time and expense of impact assessment.

The results presented here show that future research and development into improving the environmental profile of CNTs should focus both on production-side impacts and on mitigating the effects of direct CNT releases. Research on nanotechnology applications tends to emphasize new materials and structures, increasing the diversity of materials such as CNTs. On a much smaller scale, research on nanotechnology implications tends to focus on studies of releases and end-of-life exposure. Both of these research thrusts are crucial in furthering nanorelated science and technology, but the gap leaves many opportunities for important research at the intersection where we can understand and improve the environmental performance of nanomaterials production. Additionally, taking a life cycle perspective encourages balanced innovation by ensuring that novel synthesis methods that substitute a benign reagent for a toxic one, for example, do not do so at the expense of increasing toxicity from upstream processes, such as electricity production, which are shown here to dominate life cycle ecotoxicity impacts.

Model estimates of environmental impacts from CNT production are likely to change, both as a result of more comprehensive life cycle inventory data, as well as direct improvement in the efficiency of CNT manufacturing technology. Such improvements can stem from both private and public investment. Although economics will motivate the improved yields in commercial-scale CNT production modeled here, businesses may not feel strong incentives to improve on relatively low-cost items such as water use or unregulated air emissions. Research should continue to bring CNT synthesis methods in line with green chemistry principles and, ultimately, lower life cycle impacts.

A crucial policy question is how the U.S. EPA and regulatory agencies in other countries will characterize nanomaterials, and CNTs in particular. Between 2009 and 2011, the U.S. EPA issued several Significant New Use Rules (SNURs) for nanomaterials under Section 5(a)(2) of the Toxic Substances Control Act (TSCA). Each rule addresses specific CNT applications, and requires companies that intend to manufacture, import, or process CNTs to notify the U.S. EPA at least 90 days in advance. The EPA then has the burden to evaluate the intended application and to determine whether to prohibit or limit CNT use.⁶¹ Alternatively in the European Union, the 2006 Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations require the companies themselves to generate data on their chemical substances (new and existing) and assess how any risks to human health and environment can be controlled, though no rules on CNTs have been specified as yet. A functional approach based on specific applications suggests environmental modeling of CNTs as several different subclasses of substances. From a life cycle perspective, while the environmental implications of CNTs in use might be similar within a subclass, this approach will only be robust if the CNTs also incur similar impacts in manufacturing and after environmental release within a subclass. Chemical regulations typically do not specify how substances are produced, but as this work shows, non-CNT emissions from manufacturing are at least as important as exposure to the CNTs themselves in determining environmental risks. Alternately, regulations may recognize CNTs with different physicochemical properties as discrete substances, in

which case a wealth of fate, exposure, and toxicity data will need to be generated.

While nanotoxicity research strives to differentiate among the many types of CNTs after they are released into the environment, it will be crucial to link this information to their production impacts, so as to classify CNT types on a life cycle basis. Here the challenge is different: unlike toxicity information that is largely unknown, production-level records exist for each type of CNT, either in patents, reported research, or as confidential business information, and it is a matter of creating mechanisms to track and assimilate these data. As the present study shows, production-side ecotoxicity impacts of current carbonaceous nanomaterials are of at least equivalent magnitude to the impacts of their release, and only by considering the full life cycle of nanomaterials will we be comprehensive in our assessment of their benefits and risks.

■ ASSOCIATED CONTENT

§ Supporting Information

Detailed impact assessment results for emissions related to the three CNT production methods (baseline and future production efficiencies), and distributions for the Monte Carlo results. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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