

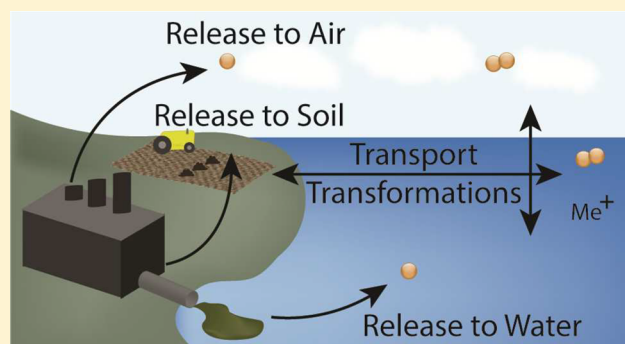
# Assessing the Risk of Engineered Nanomaterials in the Environment: Development and Application of the nanoFate Model

Kendra L. Garner,<sup>1</sup> Sangwon Suh, and Arturo A. Keller\*

Bren School of Environmental Science & Management, University of California, Santa Barbara, California 93106, United States

**S** Supporting Information

**ABSTRACT:** We developed a dynamic multimedia fate and transport model (nanoFate) to predict the time-dependent accumulation of metallic engineered nanomaterials (ENMs) across environmental media. nanoFate considers a wider range of processes and environmental subcompartments than most previous models and considers ENM releases to compartments (e.g., urban, agriculture) in a manner that reflects their different patterns of use and disposal. As an example, we simulated ten years of release of nano CeO<sub>2</sub>, CuO, TiO<sub>2</sub>, and ZnO in the San Francisco Bay area. Results show that even soluble metal oxide ENMs may accumulate as nanoparticles in the environment in sufficient concentrations to exceed the minimum toxic threshold in freshwater and some soils, though this is more likely with high-production ENMs such as TiO<sub>2</sub> and ZnO. Fluctuations in weather and release scenario may lead to circumstances where predicted ENM concentrations approach acute toxic concentrations. The fate of these ENMs is to mostly remain either aggregated or dissolved in agricultural lands receiving biosolids and in freshwater or marine sediments. Comparison to previous studies indicates the importance of some key model aspects including climatic and temporal variations, how ENMs may be released into the environment, and the effect of compartment composition on predicted concentrations.



## INTRODUCTION

Engineered nanomaterials (ENMs) are a growing class of pollutants, and although there are emerging trends in their behavior and toxicity, their impacts on the environment are still relatively poorly understood.<sup>1–6</sup> The increasing use and associated emissions of ENMs creates a compelling need to understand and predict their distributions and likely environmental concentrations in order to understand their potential impacts.<sup>1,7–13</sup>

ENMs are particles for which at least one dimension falls between 1 and 100 nm in length;<sup>14</sup> though in the environment, they will transform and accumulate at different sizes and rates. ENMs can exist as single or aggregated particles and can be manufactured with various shapes, coatings, and surface functionalities making it a challenge to predict their impact on the environment. Further, nanoparticles can undergo a number of potential transformations that depend on both the properties of the ENM and the local environment, such as aggregation, dissolution, oxidation, sulfidation, and other surface alterations.<sup>15–35</sup> These transformations complicate our understanding of their long-term fate and implications.

Field measurements of ENM concentrations ([ENM]) would be valuable for assessing their environmental distribution. However, in situ measurement of ENMs does not yet provide reliable results.<sup>36–45</sup> Therefore, determining potential environmental exposure at this stage relies on model-driven and lab-based estimates of fate. Fate models for chemicals fall

generally into three classes: steady-state multimedia box models, spatial river/watershed models, and materials flow analysis (MFA) models. In all instances, the prediction is based on a framework developed for organic chemicals that relies on chemical characteristics and processes that are not applicable to ENMs.<sup>10–12,37,46–50</sup> Both steady-state fate and transport (FT) models and MFAs cannot predict the dynamic long-term environmental distribution of ENMs or easily account for variations in climate and hydrology.<sup>37,47,48</sup> Examples of all three model approaches as applied to ENMs are given in Table S1.

FT models can provide a powerful framework to help understand the behavior of pollutants in the environment. The challenge is to incorporate ENM specific processes into the model. Most existing ENM FT models<sup>15,37,47,51–56</sup> make limited use of material-specific descriptors. They are also limited with regard to the properties, transport, and transformations they include and the spatial scale and environmental compartments they consider. However, as observed in a recent study,<sup>57</sup> most models consider only steady state over a very large region, ignore stream loads resulting from surface runoff of biosolids or fertilizers containing ENMs, and do not track ENM reaction byproducts (such as the dissolved ion). Recent

Received: October 20, 2016

Revised: April 25, 2017

Accepted: April 26, 2017

Published: April 26, 2017

studies go further in accounting for material-specific descriptors and account for the dynamic behavior of ENMs,<sup>50,58–61</sup> however, these generally focus on one specific subset of the environment, usually water and sediments, instead of a comprehensive assessment of the total environment.<sup>37,57,61</sup> In addition, more recent models attempt to incorporate a spatial component; though again, these tend to focus on a single river and its surrounding environment, and they are not easily applied to other rivers.<sup>37,53,57,60–62</sup> The spatially explicit FT models require considerable input data (e.g., river cross sections, initial sediment bed depth, river bank erosion estimates, landscape inputs, etc.) and temporal data for calibration (e.g., flow gauges in the river and tributaries, sediment bed depth over time, suspended sediments, water quality), which may not be easily available for other locations.<sup>57,61,62</sup> Higher spatial and temporal resolution is gained but at the cost of significant complexity.

The three model classifications require different model inputs and focus on different priorities. The multimedia models consider release, transport, and fate in the atmosphere, waterbodies, and the landscape (soils) with varying numbers of environmental compartments considered.<sup>47–49</sup> Transfer from one compartment to another is process based and, in some cases, limited by the rate of mass transfer. They are used for screening assessments of likely ENM concentrations. River models focus on point source release into the river and then model ENM transport and fate down gradient,<sup>37,57,60</sup> except Dale et al.,<sup>57</sup> which also considers biosolids application in several land uses. Their value is in the consideration of the spatial nature of ENM transport within the river, which provides additional insights. MFAs apply transfer coefficients to move mass from one compartment to another at a given rate, generally without considering the mechanics of the transfer process.<sup>10–12,46,52,53,63,64</sup> Since nanoFate falls within the multimedia models, we discuss the differences with similar models (i.e., MendNano and SimpleBox4Nano) in more detail.<sup>47,48</sup>

MendNano includes air, water, soil, sediment, and terrestrial and aquatic biota. However, the model is limited with regards to mass transfer processes between soil and water, uses simplified ENM transformation processes, excludes climate variability, and does not make distinctions between sub-compartments within each major compartment (for example, soil solids and soil water within soil). Only one water chemistry (i.e., freshwater or marine) and one soil type can be modeled. Runoff is modeled as a simple transfer. SimpleBox4Nano considers the transfer of ENMs in air, surface water, soil, and sediment.<sup>48</sup> Processes are modeled using first-order rate constants for all processes.<sup>48</sup> Only one water chemistry and one soil type is considered. SimpleBox4Nano tracks three nanoparticle states: (1) freely dispersed; (2) ENMs heteroaggregated with natural colloidal particles (<450 nm); (3) ENMs attached to larger natural particles (>450 nm).<sup>48</sup> However, dissolution is only modeled as a loss mechanism, and the soil compartment is still quite simplified. Neither model tracks dissolved ions. Table S1 provides more details on the differences between all types of ENM fate models.

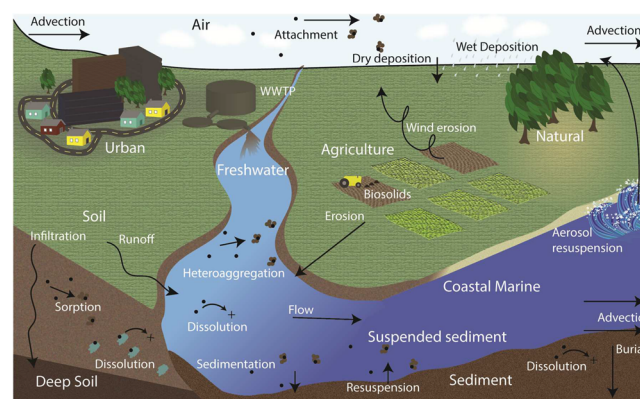
To overcome some of these limitations, nanoFate considers a wider range of ENM processes, including emissions to air, water (freshwater and marine), and soils (urban, agricultural, undeveloped) from their manufacturing, use, and disposal; advection in and out of main environmental compartments; rate-limited transport across compartments; resuspension to air

and attachment to aerosols; transformation into other ENMs or compounds; in natural waters aggregation, sedimentation, dissolution, filtration, and sorption to suspended particles and the subsequent deposition to sediment.<sup>65–69</sup> Since some ENMs also dissolve over time, nanoFate accounts for long-term accumulation of both nanoparticles and dissolved metal ions.<sup>16</sup> nanoFate is also designed to allow for the inclusion of other key transformations processes (e.g., oxidation, sulfidation, adsorption of natural organic matter, loss of the original coating) that alter their chemical properties and environmental behavior, though these are not yet sufficiently understood to incorporate into a mathematical model.<sup>1,37,70,71</sup>

nanoFate is unique because of (i) the type and structural detail of compartments included; (ii) the inclusion of key fate processes, discussed above, that have not previously been considered collectively in one model; (iii) the approach taken to calculate fate and transport rates in the face of limited data and mechanistic uncertainty. In addition, because of the rapid progress being made in ENM production and applications, we explore a range of release scenarios and corresponding long-term [ENM] estimates. nanoFate will be publically available and has been developed with extensibility to other environments, ENMs, and for additional processes.

## METHODS

nanoFate predicts the fate of ENMs in the atmosphere (including air and aerosols), soils (including urban, natural, agricultural with and without applied biosolids) divided into surface soil solids and pore water, and deep soil compartments, water (including freshwater, coastal water, and suspended sediment in both), and freshwater and coastal marine sediments (Figure 1). nanoFate simulates ENM transformations and



**Figure 1.** Conceptual model with compartments, major transfers, and transformations used in nanoFate.

transfers between compartments, tracking three ENM states: (i) free nanoparticles and small homoaggregates; (ii) ENM particles heteroaggregated with aerosols or suspended sediments; (iii) ENM dissolution products in the various waters. We assume intracompartamental transport is instantaneous resulting from assumed homogeneous distribution of ENMs within each compartment. We account for intercompartmental transport through advection and rate-limited mass transfer. As summarized in Figure 1, nanoFate calculates transfers between compartments using mass transport functions via distinct processes including attachment to aerosols from air, wet and dry deposition (from air and via aerosols), advection by wind,

runoff and erosion during precipitation events, heteroaggregation to suspended sediment, sedimentation of ENMs and suspended sediment, dissolution in water columns and sediments, flow of water and sediments from freshwater into coastal areas, advection out of the coastal zone, resuspension and burial in sediment, wind erosion from surface soil, splash back from seawater in coastal zones, transfer between soil solids and soil pore water, sorption to soil particles, dissolution in soil pore water, and transfer to deep soil. Process details are in the [Supporting Information User Guide \(SIUG\), Section 2](#). The user can adjust ENM-specific transformation rates based on specific ENM characteristics (e.g., size, surface area, coatings). Differential equations express concentration changes over time (mass transfer equations in [SIUG, Section 3](#)). We consider a daily time step and nonsteady state, to describe [ENM] variability due to seasonal weather, flow-dependent patterns, and release fluctuations.<sup>72</sup>

nanoFate considers compartment dimensions and characteristics (e.g., water chemistry, soil properties) and incorporates observed daily hydrometeorological data for precipitation, wind speed, and river flow, which improves the regional specificity of the model. nanoFate accounts for differences in freshwater and coastal water chemistry that affect ENM processes.<sup>37,47,48,50,52,60–62,73,74</sup> Organic chemical FT models consider partitioning coefficients (e.g., Henry's constant, octanol–water partitioning),<sup>66</sup> which are not applicable for most ENMs.<sup>75–77</sup> Instead, ENMs transfer continuously from one compartment to another at a rate controlled by ENM specific processes and [ENM].<sup>77,78</sup>

San Francisco Bay was selected as an initial case study region because locally specific release predictions for a range of nanomaterials were available.<sup>7</sup> The region consists of 14 419 km<sup>2</sup> divided into freshwater (11.1%), marine (1.2%), urban (24.2%), agricultural (11.1%), and undeveloped natural lands (52.5%) ([Figure S1](#)). The Bay itself, though estuarine in nature, was assigned to the freshwater compartment because of limitations in data availability for ENM processes in estuarine waters. In addition, because of complexity in modeling estuarine mixing and tidal zones, we assume separate and homogeneous freshwater and marine compartments with no mixing zone. The region was defined on the basis of USGS HUC8 watersheds ([Figure S2](#)).<sup>79</sup> In addition, given the design of the model, the region could be adapted to model a different set of water compartments, such as estuarine and marine, provided the necessary ENM-specific data were available. Temporal data extended over ten years from 2005 to 2014. [Table S2](#) provides the environmental parameters, along with estimated uncertainty for each parameter, and [Figure S3](#) shows the climate data.

Constant daily ENM release estimates from production, use, and disposal were routed to the corresponding bulk compartments (air, water, and soil),<sup>7</sup> except in alternative scenarios for an accidental spill and increasing production and release ([Table S3](#)).<sup>7</sup> ENM release via treated wastewater effluent was 46% to freshwater and 54% to coastal, on the basis of actual treated effluent flows in the area.<sup>80</sup> ENMs in biosolids are directly applied only to agricultural crops allowed to receive biosolids (~5% of total agricultural soil within the region).<sup>81</sup> Other agriculture only receives ENMs via atmospheric deposition.

Scenarios considered include (1) low and (2) high-end ENM release estimates ([Table S3](#)); (3) high estimate increased by a factor of 10; (4) 10% annual increase based on high-end release estimate; two accidental spill scenarios hypothesized to occur

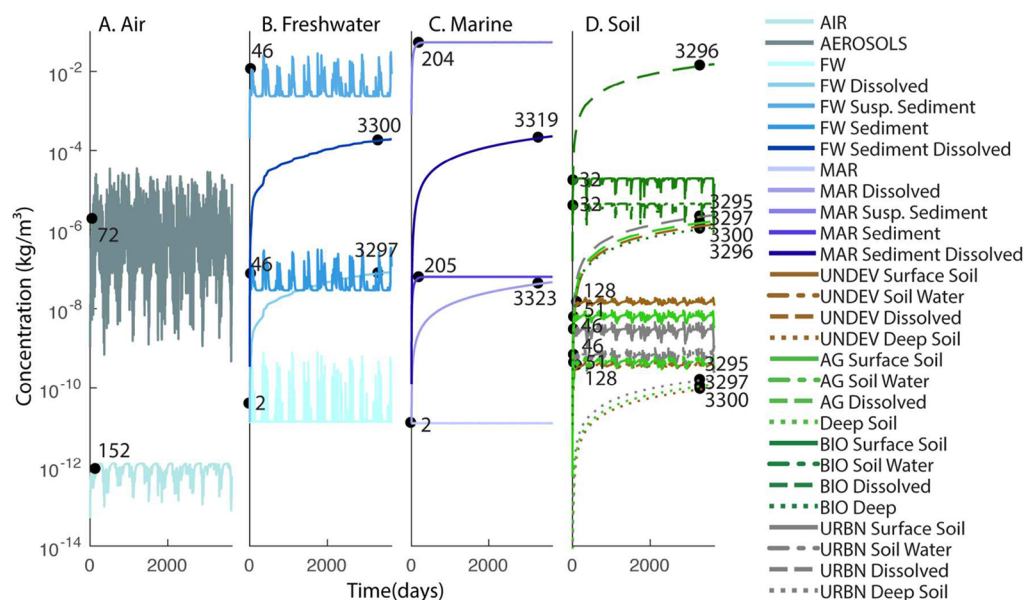
on Jan 1, 2013 with the high daily release scenario in the background: (5) 1000 kg to freshwater and (6) 1000 kg to urban soils. Data to parametrize the processes for different ENMs were collected from the available literature; rate constants were estimated for each ENM ([Table S4](#), with an indication of uncertainty). Key nanospecific rates include heteroaggregation, sedimentation, attachment and detachment to soil particles, and chemical transformations such as dissolution, for a range of environments and characteristics for each environment.<sup>1</sup> Many of these parameter values are specific to the ENM and the environmental medium; all observed data are presented in [Table S5](#).<sup>13</sup> Major sources of uncertainty include (i) scenario uncertainty in selection of the geography, (ii) measurement uncertainty in the climate data, and (iii) parameter uncertainty in chemical characteristics and the geographic data. We discuss all major sources of uncertainty in greater detail in the [Supporting Information](#).

Aggregation, dissolution, and other surface transformations of ENMs result in transfer to new forms or chemical species. We assume that once a nanoparticle has aggregated, dissolved, and/or adsorbed to other particulate matter, the transfers are not reversible and are thus tracked as separate species. Homoaggregation after release is assumed negligible relative to heteroaggregation at realistic environmental [ENM] and [suspended particles] and, thus, only include heteroaggregation ([SIUG, Section 2.3.1](#)).<sup>15,17–20,82,83</sup> We follow the approach provided by Praetorius et al. and Quik et al. to model heteroaggregation as a pseudo-first order process relative to current water and suspended sediment concentrations.<sup>37,59</sup> We do not assume that complete heteroaggregation occurs as studies have shown that nanoscale particles can be present in surface waters.<sup>84,85</sup>

In the air, ENM attachment to aerosols or suspended sediments is assumed to be irreversible. Deposition is calculated for free ENMs and ENMs in aerosols. Dry deposition is calculated using Stokes' Law ([SIUG, Section 2.1.1](#)).<sup>86</sup> Wet deposition of aerosols considers the scavenging ratio developed by Mackay<sup>66</sup> and an additional factor of 0.01 for raindrop scavenging of nanoparticles ([SIUG, Section 2.1.2](#)), since 10 nm and smaller particles can have a scavenging ratio of up to 2 orders of magnitude smaller than those in the 1–5  $\mu\text{m}$  range.<sup>87</sup> Free and aerosol-associated ENMs can be transported in or out of the air compartment via wind ([SIUG, Section 2.1.3](#)). Since heteroaggregation of ENMs with aerosols has not been studied for specific ENMs, the rate of heteroaggregation in air is reduced by a factor of 1000 because the collision frequency is assumed to be lower in air resulting in fewer particle interactions that result in heteroaggregation ([SIUG, Section 2.1.4](#)).<sup>1</sup>

Aerosolization of ENMs from coastal splash and resuspension of ENMs attached to surface soil particles by wind events result in transfer back to the aerosols compartment. Transport from seawater to the aerosol compartment was computed using a flux equation that relies on enrichment factors of trace metals,<sup>88–95</sup> which we assume is comparable to that of their ENM counterparts ([SIUG, Section 2.3.5](#)). For wind erosion of surface soil, we use the saltation equation and the vertical flux conversion to estimate total transport of soil particles to aerosols ([SIUG, Section 2.2.1](#)).<sup>96–99</sup>

Deposition of suspended sediment (and attached ENMs) was estimated using Stokes' Law ([SIUG, Section 2.3.2](#)), considering suspended particle density, fluid (freshwater vs. marine) density and dynamic viscosity, and



**Figure 2.** ZnO accumulation across environmental media, including (A) air, (B) freshwater, (C) marine water, and (D) soil under the low-end daily release scenario over ten years of model simulation. In this run, initial concentrations are zero in all media, which can be modified by the user. Black dots indicate time to reach steady state as indicated by reaching 95% of the average during the final year of simulation. FW = freshwater, MAR = marine, UNDEV = undeveloped (natural) lands, AG = agriculture without biosolids application, BIO = agriculture with biosolids application, and URBN = urban lands. Pseudosteady state, where [chemical] is generally stable except for deviations caused by climate variables, is reached for many of the water and particulate compartments within the first year (air and aerosols reach pseudosteady state the fastest, and the marine suspended sediment, sediment, and soils reach pseudosteady state the slowest). The dissolved and deep soil compartments do not stabilize within the 10-year time frame.

[ENM]<sub>suspended particle</sub><sup>66</sup> Sedimentation of free nanoparticles and small homoaggregates considers rate constants from published sedimentation studies for corresponding media (SIUG, Section 2.3.3).<sup>18,19,26,100–103</sup>

Visual MINTEq (version 3.1)<sup>104</sup> was used to predict metal speciation in freshwater, marine, and soil water, considering specific water chemistries. Maximum equilibrium dissolution was established for a given ENM in each specific water (SIUG, Section 2.3.4; Figure S6 presents the maximum solubility at a given initial concentration and pH). Experimental dissolution rate data in the specific water chemistry was obtained for each ENM and modeled using an assumed first-order rate process that proceeds until the equilibrium ion concentration is reached (Table S4).<sup>105</sup> Since there is no experimental data for dissolution of ENMs in freshwater and marine sediments, the rate of dissolution was assumed to be 1/10th the rate in the corresponding water column, considering mass transfer is slower in porous media.<sup>66,68,106</sup>

Transfer of ENMs and suspended sediment from freshwater to coastal waters and the transfer from coastal waters to the marine compartment (out of the modeled system) is considered an advective flux, estimated using regional flow data (SIUG, Section 2.3.6). The advective flux of ENMs associated with suspended sediment is dependent on the flow of water and concentration of suspended sediment in water. The advective flux of ENMs in sediment via bedload transport is assumed to depend on water flow rate. ENM mass in sediments is calculated on the basis of additions by sedimentation and losses from resuspension and burial (SIUG, Sections 2.4.1 and 2.4.2). Once an ENM is associated with particulate matter, we assume that it will remain associated with that particulate matter: in sediment, all ENMs are

associated with sediment, and transfer between compartments is exclusively via sediment processes.<sup>37</sup>

Runoff and erosion during storm events allow for transfer from the landscape to receiving waters. Infiltration transports ENMs to the soil compartments and their corresponding waters. Runoff was calculated using the United States Department of Agriculture's (USDA) Soil Conservation Service (SCS) runoff equation, which uses the USDA's Natural Resources Conservation Service (NRCS) curve number. The curve number indicates the amount of runoff or infiltration that will occur during a precipitation event (SIUG, Section 2.2.2).<sup>107</sup> Soil loss resulting from erosion was calculated using the Revised Universal Soil Loss Equation (RUSLE), which accounts for precipitation amount, soil erodibility, regional slope, cover management, and support practices (SIUG, Section 2.2.3). Dissolution of ENMs in soil water was assumed to occur at the same rate as in groundwater studies (SIUG, Section 2.2.6). Leaching transfers ENMs from surface to deep soils using the default leaching rate reported in Mackay (SIUG, Section 2.2.5).<sup>66</sup>

Retention of ENMs in the soil as they are transported via soil pore water is modeled using experimental breakthrough curve data, where possible (SIUG, Section 2.2.4).<sup>27,108–130</sup> We do not consider a maximum attachment capacity in soils, even with continuous and increasing ENM application via biosolids or from the atmosphere, due to a lack of experimental data. However, posthoc analysis of several extreme scenarios indicates that current ENM application rates are very unlikely to exceed maximum attachment capacity.

To estimate the risk to ecosystems, predicted [ENMs] from the various release scenarios were compared to species sensitivity distributions (SSDs) for freshwater and soil systems where available and to individual species end points, e.g., no

observed effect concentration (NOEC) or lethal concentration ( $LC_{50}$ ), when SSDs were not available.<sup>12,96</sup> We used two toxicity thresholds, the no observed adverse effect level (NOAEL) and the lethal concentration required to kill 50% of the population ( $LC_{50}$ ), to calculate the 5% hazardous concentration ( $HC_5$ ).<sup>64,131–134</sup> This threshold was then compared to the predicted exposure concentration (PECs).

## RESULTS

**Predicted Exposure Concentrations.** In a few weeks, even under the low-end release scenario and regardless of the entry point to the environment, ENMs transfer to all environmental compartments. The highest accumulation can be found in aerosols, in freshwater and marine suspended sediment and sediment beds, dissolved in sediment, and in agricultural surface soil solids (Figure 2 for ZnO; Figures S7–S9 for CeO<sub>2</sub>, CuO, and TiO<sub>2</sub>). ZnO is presented here because of high production volumes, known toxicological impacts, and its solubility, used to highlight the capabilities of nanoFate. Heteroaggregation is generally the dominant process, transferring ENMs from bulk compartments (air, water, soil) to the mineral particles. The magnitude of these transfers for compartments without direct releases is, however, generally low, ranging from less than 1 pg d<sup>-1</sup> up to several g d<sup>-1</sup>. For nano ZnO and CuO, there is also substantial dissolution in the water column and sediment for freshwater and marine systems (Figure 2B,C for ZnO; Figure S8B,C for CuO). To demonstrate the importance of dissolution, eliminating dissolution from sediment results in an increase in sediment concentrations of more than 2 orders of magnitude (Figure S5).

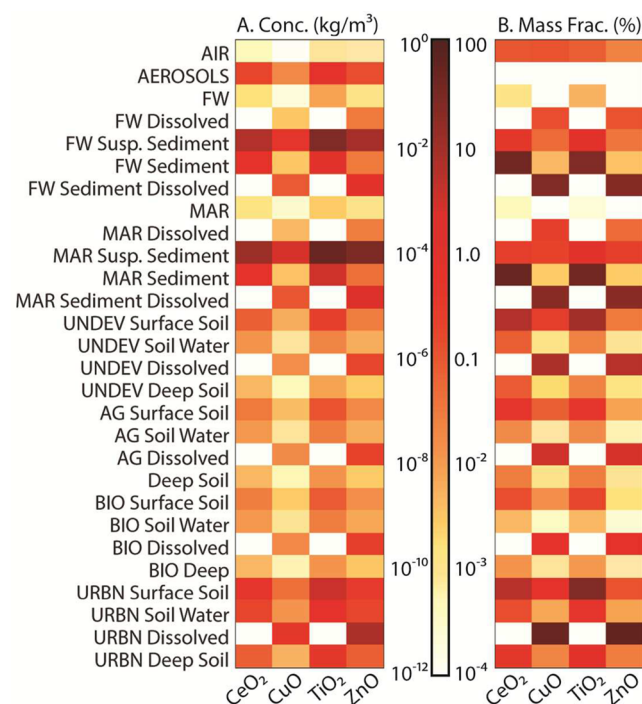
Since there is a significant probability that ZnO will dissolve substantially during wastewater treatment, an additional scenario based on the high release was explored assuming only 10% would enter as ENM and 90% as Zn<sup>2+</sup> (Figures S11 and S12).<sup>135–138</sup> While both  $[ENM]_{\text{freshwater}}$  and  $[ENM]_{\text{freshwater suspended sediment}}$  decreased (Figure S11A,B) because releases as ENM were lower, the decrease was greater for suspended sediment (Figure S12), due to less aggregation resulting from lower concentrations and more free/small aggregates. This indicates that toxic levels will depend heavily on ENM speciation as released and in the compartment.

Most compartment concentrations vary less than 15% for all ENMs by the final year of each scenario. The exceptions are aerosols and freshwater suspended sediment where the natural fluctuation of environmental processes (e.g., precipitation, runoff) and heteroaggregation cause substantial variability. These temporal variations result in intra-annual concentrations fluctuations of up to 3 orders of magnitude. Though less visible, the concentration does fluctuate in apparently steady compartments such as marine waters (Figure S4). Soils exhibit the highest long-term relative increase in concentration, though concentrations are generally not as high as previous studies predicted, likely because nanoFate allows for loss to a deeper soil compartment and dissolution.<sup>10–12,48</sup> Exploration of different release scenarios shows that release amount can cause orders of magnitude differences in the predicted environmental concentrations over time (Figures S10 and S13–S16).

Compartments with substantial fluctuations in concentration are important for two reasons: (1) any single day with a sharp increase in concentration could result in short-term toxicity; (2) seasonal trends can be seen from these daily variations that

could have short-term impacts if the release of ENMs also corresponds with the seasonal variations. For example, if the release of an ENM also varies by season (e.g., higher concentrations tend to accumulate in aerosols in summer and higher environmental releases in summer, see Figure 2), there may be seasonal/cyclical toxicity peaks.

Although the mass of ENMs associated with particulate compartments (aerosols, freshwater suspended sediment, marine suspended sediment) relative to the total mass of ENMs in the environment (i.e., mass fraction) is small, these compartments have the highest predicted  $[ENM]$  (Figure 3).



**Figure 3.** (A) Average long-term concentration of ENMs by compartments under the high release scenario; (B) final mass fractions after 10 years.

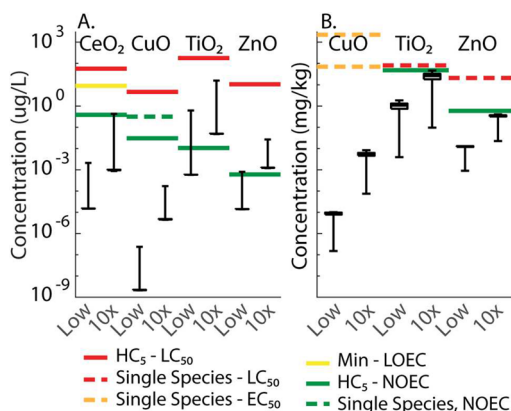
Dissolved Zn concentrations are also predicted to be relatively high. The model predicts several orders of magnitude higher  $[ENM]$  in agricultural soils to which biosolids are applied than to other soils receiving only atmospheric deposition. ENM loading to urban soils may be revised as better estimates for release of ENMs from paints and coatings used in buildings and transportation are developed, but they are unlikely to reach the levels of agricultural biosolids. Overall, the fate of many ENMs is associated mostly with agricultural lands receiving biosolids and freshwater or marine sediments, either aggregated (homo and hetero) or in dissolution products.

For each release scenario, the average concentration in each compartment is calculated over the final year of a model run. In a comparison across the release scenarios, the low-end release scenario tends to result in concentrations that are mostly 1 order of magnitude lower, though occasionally up to 3 orders of magnitude lower than the high release scenario (Figures S17–S20). There is not much difference between the constant-level high release scenario, the increasing high release scenario, and the high release scenarios with accidental spills for ZnO (Figures S13–S16 and S17A) as well as for the other ENMs. The impact of an accidental spill is visible in the increased mass

fractions though there is no substantial change in the environmental concentration at the end of the simulated period (Figures S15, S16, and S17A). Increasing the high release scenario by a factor of 10 increases the environmental concentrations by slightly more than an order of magnitude, though this is limited in scenarios where the equilibrium dissolution concentration is reached (Figures S14 and S17A). These increases are not always proportional because of advective losses from the system and concentration-dependent dissolution rates.

A comparison across ENMs indicates how important the release estimates are to the resulting long-term concentrations across most compartments. For example, because  $\text{TiO}_2$  is produced and released in far higher quantities than any of the other ENMs in this study, the resulting long-term concentrations are much higher than  $\text{CuO}$ , whose estimated release is several orders of magnitude lower. In addition, release patterns to air, water, and agricultural soils vary by ENM due to differences in how ENMs are used in various applications (e.g., paints, personal care products, fuel catalysts, pesticides). For the soluble ENMs ( $\text{CuO}$  and  $\text{ZnO}$ ), there is also a significant amount of dissolution in freshwater, marine, and agricultural soil water, which can result in the formation of  $\text{Cu}$  and  $\text{Zn}$  precipitates. Conversely, the white blocks in the  $\text{CeO}_2$  and  $\text{TiO}_2$  columns indicate that no or minimal dissolution of these ENMs occurs in the water and soil water compartments.

**Risk Assessment.** A comparison of long-term concentrations in freshwater environments with predicted hazardous concentrations at which 5% of species in a freshwater ecosystem will be harmed ( $\text{HC}_5$ ) indicates that even under the highest release scenario considered in this study  $\text{CeO}_2$  will likely be well below the NOEC and the lowest observed effect concentration (LOEC) (Figures 4 and S22A).<sup>133</sup> Under all release scenarios,  $\text{CuO}$  does not exceed the NOEC  $\text{HC}_5$  (Figure S22B). The single species NOAEC line (light green line, *D. magna*) indicates that under the considered scenarios it



**Figure 4.** Comparison between the range of predicted daily (A) freshwater concentrations and (B) soil concentrations and several toxicity end points above which a toxic effect would be observed for 5% of species in a freshwater ecosystem: the NOEC, LOEC,  $\text{LC}_{50}$ , or  $\text{EC}_{50}$ . Each box and whiskers plot shows the range in daily concentrations for each release scenario with the mean depicted as a black horizontal line. Because the graphic shows such a wide range in environmental concentrations, the full boxes are difficult to visualize although the boxplot includes the full set of quantiles (2.5%, 25%, 50%, 75%, 97.5%). SSDs not already published in the literature are presented in Figure S21.

is still unlikely that toxic effects would be observed in freshwater except in the highest release scenario considered (Figure S22B).<sup>134</sup>  $\text{TiO}_2$  and  $\text{ZnO}$  will occasionally exceed the freshwater NOEC  $\text{HC}_5$  in all scenarios and every day for the highest release scenario (Figure S22C,D).<sup>132</sup>  $\text{ZnO}$  poses the highest concern because, under all release scenarios (including the lowest predicted releases), freshwater concentrations may exceed the NOEC  $\text{HC}_5$ , indicating that some effect from  $\text{ZnO}$  may already be noticeable in the San Francisco Bay for the most sensitive species.<sup>132</sup> In addition, on the basis of a comparison of SSDs to predicted concentrations of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , these ions are predicted to cause toxicity to sensitive species (Figure S23).

In agricultural and urban soils, neither  $\text{TiO}_2$  nor  $\text{ZnO}$  exceeds the NOEC for soil ecosystems even under the most extreme release scenarios, though both are quite close in the highest release scenario for agricultural soils with biosolids (Figures 4 and S24).<sup>132</sup>  $\text{CuO}$  is many orders of magnitude below the  $\text{EC}_{50}$  for soil microbe growth inhibition (Figure S24A).<sup>124,139</sup>  $\text{CeO}_2$  was not included in this graph because no specific toxic end points for soil organisms could be identified in the literature for comparison. In soils without direct application of ENMs, concentrations are likely to be two or more orders of magnitude lower than the NOEC. However, typical background concentrations of  $\text{Zn}$  range from 10 to 300  $\text{mg Zn kg}^{-1}$  soil,<sup>140,141</sup> which is substantially higher than the predicted concentrations of  $\text{ZnO}$  in the model.

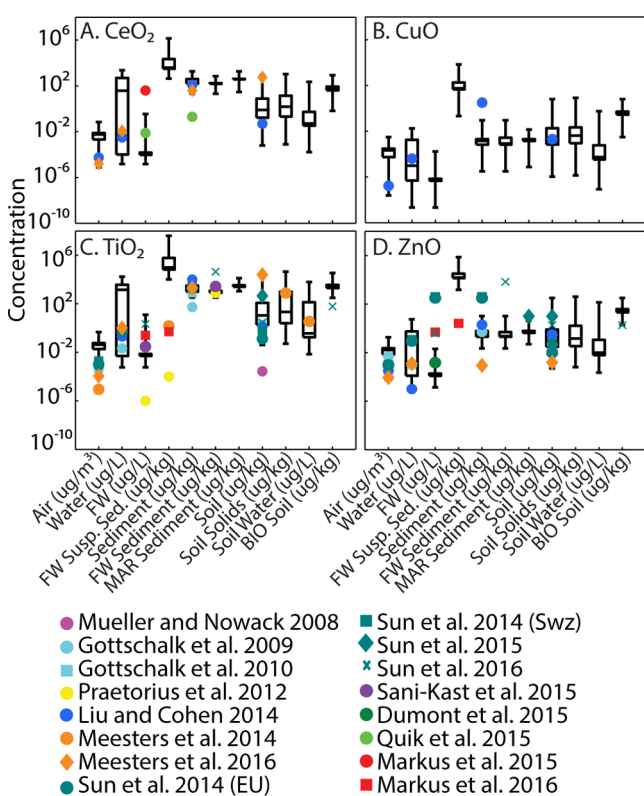
## DISCUSSION AND ENVIRONMENTAL SIGNIFICANCE

Our results point to several significant findings: (1) Soluble nanoparticles, such as  $\text{ZnO}$  and  $\text{CuO}$ , can accumulate in the aquatic environment over the long-term in sufficient concentrations to potentially cause toxicity (as observed for the freshwater ecosystem), even accounting for dissolution in aquatic media. Solubility, often assumed to be a primary driver of ENM toxicity, is not the only determining factor for toxicity (e.g., other drivers include oxidative stress, cationic injury to membranes, reactive oxygen species production, and cell membrane lysis by surface reactivity).<sup>142</sup> (2) The highest concentrations and mass fractions of ENMs will be found in agricultural soils to which biosolids are applied and freshwater and marine sediments, which continue to increase slowly over time; aerosol and suspended sediment concentrations are also high, but their mass fraction is always quite small. (3) If production and release of  $\text{TiO}_2$  into the environment continues to increase, PECs may likely exceed observed toxicity thresholds. (4) Even at very low release volumes, such as with  $\text{CuO}$ , the nanoparticle itself may still reach localized toxic concentrations regardless of solubility. (5) Environmental fluctuations (e.g., rainfall) and release fluctuations (e.g., accidental spills) have the potential to cause short-term toxic effects. Steady state FT or MFA models are unable to predict these spikes in daily concentrations. Accidental releases can cause temporary spikes in environmental concentrations that may cause localized short-term toxicity but do not appear to cause significant long-term concentration increases at the regional level. However, if current releases increase and a substantial spill occurs, the effects would be of concern, primarily for  $\text{ZnO}$  and secondarily for  $\text{TiO}_2$  and  $\text{CuO}$ .<sup>54</sup> In addition, while air PECs are generally low under these specific scenarios, localized releases that result in ambient concentration

spikes may cause chronic toxic effects in humans and animals.<sup>143</sup>

Models are always simplifications developed for specific objectives. In this case, the objective was to evaluate the large-scale regional fate of specific ENMs and provide a rapid-screening tool. Given that we explored large-scale release scenarios, no model validation is currently feasible because of a lack of experimental data designed to cover the range of environmental conditions in a large-scale fate model and a lack of field observations against which one could compare the results.<sup>13</sup> In fact, there is a lack of field data even at small scales to validate ENM FT models.<sup>13</sup>

Instead, we compare nanoFate model PECs to previous studies (Figure 5). For CeO<sub>2</sub>, nanoFate PECs are on the low-



**Figure 5.** Comparison between nanoFate model results and other predictions from MFAs<sup>10–12,46,52,62,73</sup> and mechanistic fate models.<sup>37,47–50,60,61,74</sup> Comparisons are for (A) CeO<sub>2</sub>, (B) CuO, (C) TiO<sub>2</sub>, and (D) ZnO. nanoFate results presented as a box and whiskers plot which includes the full range of predicted concentrations from all release scenarios. Units for concentrations in *x*-axis labels.

end of two previous predictions for freshwater but are quite similar for all the other environmental compartments (Figure 5A).<sup>47,50,60</sup> For CuO, our range in predictions for most compartments overlaps previous studies, though we predict slightly higher air concentrations and slightly lower sediment concentrations than other models, since we included dissolution in sediment (Figure 5B).<sup>47</sup> The range in previous TiO<sub>2</sub> PECs is quite wide (Figure 5C).<sup>37,47–49,52,61,73,74,144</sup> nanoFate results fall within this range, except in suspended sediment and biosolids-agricultural soils where our results tend to be somewhat higher, due to our more realistic assumption that biosolids are only applied to a fraction of agricultural lands. For ZnO, our predictions fall within previous predicted ranges except for suspended sediment, where nanoFate predicts much

higher concentrations, and somewhat lower than previous predictions in the freshwater column and in marine sediment (Figure 5D).<sup>47,49,52,61,62</sup> In a spatial model, Dale et al. predict the 95th percentile total Zn from ZnO in a watershed to range from 10<sup>-8</sup> and 10<sup>-2</sup> μg/L which is similar to the range predicted by nanoFate (10<sup>-6</sup> and 10<sup>-3</sup> μg/L), even with rather different loading and spatial resolution.<sup>57</sup> nanoFate sediment [ENM] predictions tend to be on the low-end relative to previous models, resulting from the inclusion of dissolution in freshwater and marine sediment. If dissolution is set to zero, the sediment ZnO concentration increases by orders of magnitude, closer to Sun et al. (Figure S5).<sup>11,12</sup> This highlights the importance of considering dissolution. The differences between models also reflect underlying assumptions about ENM sources, release amounts, routes, and time periods.

While nanoFate considers a wider range of ENM processes as well as the fate of transformation products, there is still a need for more experimental investigations designed to determine medium-dependent process rates since the uncertainty in parameter values is considerable.<sup>13</sup> In addition, while the model does predict a range of many orders of magnitude for all environmental compartments, the addition of a spatial component would likely increase the range of predicted concentrations as seen in Dale et al.<sup>57</sup> This is more likely to be relevant for short-term PEC estimates, which may vary considerably. The predicted long-term accumulation is likely to be more accurate, because the long-term averages do not change substantially as a result of a moderate change in transfer or transformation rates.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05279.

nanoFate User Guide (PDF)

5 supplemental tables providing the parameters for the San Francisco Bay case study and uncertainty; 24 figures providing additional model results for the San Francisco Bay case study (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*Phone: 805-893-7548; e-mail: [keller@bren.ucsb.edu](mailto:keller@bren.ucsb.edu).

### ORCID

Kendra L. Garner: 0000-0001-7167-8490

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation (NSF) and the Environmental Protection Agency (EPA) under Cooperative Agreement Number DBI 0830117 and under Assistance Agreement No. 83557901 awarded by the U.S. Environmental Protection Agency to the University of California, Santa Barbara. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of NSF or EPA. This was not subjected to EPA review and no official endorsement should be inferred.

## REFERENCES

- (1) Garner, K.; Keller, A. Emerging Patterns for Engineered Nanomaterials in the Environment: A Review of Fate and Toxicity Studies. *J. Nanopart. Res.* **2014**, *16*, 2503.
- (2) Cornelis, G.; Hund-Rinke, K.; Kuhlbusch, T.; van den Brink, N.; Nickel, C. Fate and Bioavailability of Engineered Nanoparticles in Soils: A Review. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44* (24), 2720–2764.
- (3) Peijnenburg, W. J. G. M.; Baalousha, M.; Chen, J.; Chaudry, Q.; Von der kammer, F.; Kuhlbusch, T. A. J.; Lead, J.; Nickel, C.; Quik, J. T. K.; Renker, M.; et al. A Review of the Properties and Processes Determining the Fate of Engineered Nanomaterials in the Aquatic Environment. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45* (19), 2084–2134.
- (4) Bour, A.; Mouchet, F.; Silvestre, J.; Gauthier, L.; Pinelli, E. Environmentally relevant approaches to assess nanoparticles ecotoxicity: A review. *J. Hazard. Mater.* **2015**, *283*, 764–777.
- (5) López-Serrano, A.; Muñoz Olivas, R.; Sanz Landaluze, J.; Cámara, C. Nanoparticles: a global vision. Characterization, separation, and quantification methods. Potential environmental and health impact. *Anal. Methods* **2014**, *6* (1), 38–56.
- (6) Dwivedi, A. D.; Dubey, S. P.; Sillanpää, M.; Kwon, Y.-N.; Lee, C.; Varma, R. S. Fate of engineered nanoparticles: Implications in the environment. *Coord. Chem. Rev.* **2015**, *287*, 64–78.
- (7) Keller, A. A.; Lazareva, A. Predicted releases of engineered nanomaterials: From global to regional to local. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 65–70.
- (8) Keller, A. A.; McFerran, S.; Lazareva, A.; Suh, S. Global life cycle releases of engineered nanomaterials. *J. Nanopart. Res.* **2013**, *15* (6), 1–17.
- (9) Gottschalk, F.; Nowack, B. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* **2011**, *13* (5), 1145.
- (10) Sun, T. Y.; Gottschalk, F.; Hungerbühler, K.; Nowack, B. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. *Environ. Pollut.* **2014**, *185*, 69–76.
- (11) Sun, T.; Conroy, G.; Donner, E.; Hungerbühler, K.; Lombi, E.; Nowack, B. Probabilistic modelling of engineered nanomaterial emissions to the environment: a spatio-temporal approach. *Environ. Sci.: Nano* **2015**, *2*, 340–351.
- (12) Sun, T.; Bornhöft, N. A.; Hungerbühler, K.; Nowack, B. Dynamic Probabilistic Modelling of Environmental Emissions of Engineered Nanomaterials. *Environ. Sci. Technol.* **2016**, *50* (9), 4701–4711.
- (13) Baalousha, M.; Cornelis, G.; Kuhlbusch, T.; Lynch, I.; Nickel, C.; Peijnenburg, W.; van den Brink, N. Modeling Nanomaterials Fate and Uptake in the Environment: Current Knowledge and Future Trends. *Environ. Sci.: Nano* **2016**, *3*, 323–345.
- (14) Hatto, P. ISO consensus definitions relevant to nanomaterials and nanotechnologies. In *4th Annual Nano Safety for Success Dialogue*, Brussels, March 20 and 30, 2011.
- (15) Quik, J. T. K.; Velzeboer, I.; Wouterse, M.; Koelmans, A. A.; van de Meent, D. Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Water Res.* **2014**, *48*, 269–279.
- (16) Stebounova, L.; Guio, E.; Grassian, V. Silver nanoparticles in simulated biological media: a study of aggregation, sedimentation, and dissolution. *J. Nanopart. Res.* **2011**, *13* (1), 233–244.
- (17) Thio, B. J. R.; Zhou, D.; Keller, A. A. Influence of natural organic matter on the aggregation and deposition of titanium dioxide nanoparticles. *J. Hazard. Mater.* **2011**, *189* (1–2), 556–563.
- (18) Zhou, D.; Keller, A. A. Role of morphology in the aggregation kinetics of ZnO nanoparticles. *Water Res.* **2010**, *44* (9), 2948–2956.
- (19) Keller, A. A.; Wang, H.; Zhou, D.; Lenihan, H. S.; Cherr, G.; Cardinale, B. J.; Miller, R.; Ji, Z. Stability and Aggregation of Metal Oxide Nanoparticles in Natural Aqueous Matrices. *Environ. Sci. Technol.* **2010**, *44* (6), 1962–1967.
- (20) Conway, J. R.; Adeleye, A. S.; Gardea-Torresdey, J.; Keller, A. A. Aggregation, Dissolution, and Transformation of Copper Nanoparticles in Natural Waters. *Environ. Sci. Technol.* **2015**, *49* (5), 2749–2756.
- (21) Adam, V.; Loyaux-Lawniczak, S.; Labille, J.; Galindo, C.; del Nero, M.; Gangloff, S.; Weber, T.; Quaranta, G. Aggregation behaviour of TiO<sub>2</sub> nanoparticles in natural river water. *J. Nanopart. Res.* **2016**, *18* (1), 1–11.
- (22) Baalousha, M. Aggregation and disaggregation of iron oxide nanoparticles: Influence of particle concentration, pH and natural organic matter. *Sci. Total Environ.* **2009**, *407* (6), 2093–2101.
- (23) Badawy, A. M. E.; Luxton, T. P.; Silva, R. G.; Scheckel, K. G.; Suidan, M. T.; Tolaymat, T. M. Impact of Environmental Conditions (pH, Ionic Strength, and Electrolyte Type) on the Surface Charge and Aggregation of Silver Nanoparticles Suspensions. *Environ. Sci. Technol.* **2010**, *44* (4), 1260–1266.
- (24) Dunphy Guzman, K. A.; Finnegan, M. P.; Banfield, J. F. Influence of Surface Potential on Aggregation and Transport of Titania Nanoparticles. *Environ. Sci. Technol.* **2006**, *40* (24), 7688–7693.
- (25) Petosa, A. R.; Jaisi, D. P.; Quevedo, I. R.; Elimelech, M.; Tufenkji, N. Aggregation and Deposition of Engineered Nanomaterials in Aquatic Environments: Role of Physicochemical Interactions. *Environ. Sci. Technol.* **2010**, *44* (17), 6532–6549.
- (26) Adeleye, A.; Conway, J.; Perez, J.; Rutten, P.; Keller, A. A. Influence of extracellular polymeric substances on the long-term fate, dissolution, and speciation of copper-based nanoparticles. *Environ. Sci. Technol.* **2014**, *48* (21), 12561–12568.
- (27) Waalewijn-Kool, P. L.; Diez Ortiz, M.; van Straalen, N. M.; van Gestel, C. A. M. Sorption, dissolution and pH determine the long-term equilibration and toxicity of coated and uncoated ZnO nanoparticles in soil. *Environ. Pollut.* **2013**, *178*, 59–64.
- (28) Cornelis, G.; DooletteMadeleine Thomas, C.; McLaughlin, M. J.; Kirby, J. K.; Beak, D. G.; Chittleborough, D. Retention and Dissolution of Engineered Silver Nanoparticles in Natural Soils. *Soil Sci. Soc. Am. J.* **2012**, *76* (3), 891.
- (29) Elzey, S.; Grassian, V. Agglomeration, isolation and dissolution of commercially manufactured silver nanoparticles in aqueous environments. *J. Nanopart. Res.* **2010**, *12* (5), 1945–1958.
- (30) Levard, C.; Reinsch, B. C.; Michel, F. M.; Oumahi, C.; Lowry, G. V.; Brown, G. E. Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate. *Environ. Sci. Technol.* **2011**, *45* (12), 5260–5266.
- (31) Zhang, H.; Chen, B.; Banfield, J. F. Particle Size and pH Effects on Nanoparticle Dissolution. *J. Phys. Chem. C* **2010**, *114* (35), 14876–14884.
- (32) Li, L.; Zhu, W.; Zhang, P.; Chen, Z.; Han, W. Photocatalytic oxidation and ozonation of catechol over carbon-black-modified nano-TiO<sub>2</sub> thin films supported on Al sheet. *Water Res.* **2003**, *37* (15), 3646–3651.
- (33) Lok, C.-N.; Ho, C.-M.; Chen, R.; He, Q.-Y.; Yu, W.-Y.; Sun, H.; Tam, P. K.-H.; Chiu, J.-F.; Che, C.-M. Silver nanoparticles: partial oxidation and antibacterial activities. *JBIC, J. Biol. Inorg. Chem.* **2007**, *12* (4), 527–534.
- (34) Ma, R.; Levard, C.; Michel, F. M.; Brown, G. E.; Lowry, G. V. Sulfidation Mechanism for Zinc Oxide Nanoparticles and the Effect of Sulfidation on Their Solubility. *Environ. Sci. Technol.* **2013**, *47* (6), 2527–2534.
- (35) Thalmann, B.; Voegelin, A.; Sinnet, B.; Morgenroth, E.; Kaegi, R. Sulfidation Kinetics of Silver Nanoparticles Reacted with Metal Sulfides. *Environ. Sci. Technol.* **2014**, *48* (9), 4885–4892.
- (36) von der Kammer, F.; Ferguson, P. L.; Holden, P. A.; Masion, A.; Rogers, K. R.; Klaine, S. J.; Koelmans, A. A.; Horne, N.; Unrine, J. M. Analysis of engineered nanomaterials in complex matrices (environment and biota): General considerations and conceptual case studies. *Environ. Toxicol. Chem.* **2012**, *31* (1), 32–49.
- (37) Praetorius, A.; Scheringer, M.; Hungerbühler, K. Development of Environmental Fate Models for Engineered Nanoparticles—A Case Study of TiO<sub>2</sub> Nanoparticles in the Rhine River. *Environ. Sci. Technol.* **2012**, *46* (12), 6705–6713.
- (38) Petersen, E. J.; Flores-Cervantes, D. X.; Bucheli, T. D.; Elliott, L. C. C.; Fagan, J. A.; Gogos, A.; Hanna, S.; Kägi, R.; Mansfield, E.;



- Bustos, A. R. M.; et al. Quantification of Carbon Nanotubes in Environmental Matrices: Current Capabilities, Case Studies, and Future Prospects. *Environ. Sci. Technol.* **2016**, *50* (9), 4587–4605.
- (39) Yang, Y.; Reed, R.; Schoepf, J.; Hristovski, K.; Herckes, P.; Westerhoff, P. Prospecting nanomaterials in aqueous environments by cloud-point extraction coupled with transmission electron microscopy. *Sci. Total Environ.* **2017**, *584–585*, 515–522.
- (40) Laborda, F.; Bolea, E.; Cepriá, G.; Gómez, M. T.; Jiménez, M. S.; Pérez-Arantegui, J.; Castillo, J. R. Detection, characterization and quantification of inorganic engineered nanomaterials: A review of techniques and methodological approaches for the analysis of complex samples. *Anal. Chim. Acta* **2016**, *904*, 10–32.
- (41) Majedi, S. M.; Lee, H. K. Recent advances in the separation and quantification of metallic nanoparticles and ions in the environment. *TrAC, Trends Anal. Chem.* **2016**, *75*, 183–196.
- (42) Rodrigues, S. M.; Trindade, T.; Duarte, A. C.; Pereira, E.; Koopmans, G. F.; Römkens, P. F. A. M. A framework to measure the availability of engineered nanoparticles in soils: Trends in soil tests and analytical tools. *TrAC, Trends Anal. Chem.* **2016**, *75*, 129–140.
- (43) Wagner, S.; Gondikas, A.; Neubauer, E.; Hofmann, T.; von der Kammer, F. Spot the Difference: Engineered and Natural Nanoparticles in the Environment—Release, Behavior, and Fate. *Angew. Chem., Int. Ed.* **2014**, *53* (46), 12398–12419.
- (44) Gondikas, A. P.; von der Kammer, F.; Reed, R. B.; Wagner, S.; Ranville, J. F.; Hofmann, T. Release of TiO<sub>2</sub> Nanoparticles from Sunscreens into Surface Waters: A One-Year Survey at the Old Danube Recreational Lake. *Environ. Sci. Technol.* **2014**, *48* (10), 5415–5422.
- (45) Montañó, M. D.; Lowry, G. V.; von der Kammer, F.; Blue, J.; Ranville, J. F. Current status and future direction for examining engineered nanoparticles in natural systems. *Environ. Chem.* **2014**, *11* (4), 351–366.
- (46) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. *Environ. Toxicol. Chem.* **2010**, *29* (5), 1036–1048.
- (47) Liu, H. H.; Cohen, Y. Multimedia Environmental Distribution of Engineered Nanomaterials. *Environ. Sci. Technol.* **2014**, *48* (6), 3281–3292.
- (48) Meesters, J. A. J.; Koelmans, A. A.; Quik, J. T. K.; Hendriks, A. J.; van de Meent, D. Multimedia Modeling of Engineered Nanoparticles with SimpleBox4nano: Model Definition and Evaluation. *Environ. Sci. Technol.* **2014**, *48* (10), 5726–5736.
- (49) Meesters, J.; Quik, J.; Koelmans, A.; Hendriks, J.; van de Meent, D. Multimedia Environmental Fate and Speciation of Engineered Nanoparticles: A Probabilistic Modeling Approach. *Environ. Sci.: Nano* **2016**, *3*, 715–727.
- (50) Markus, A. A.; Parsons, J. R.; Roex, E. W. M.; de Voogt, P.; Laane, R. W. P. M. Modeling aggregation and sedimentation of nanoparticles in the aquatic environment. *Sci. Total Environ.* **2015**, *506–507*, 323–329.
- (51) Arvidsson, R.; Molander, S.; Sandén, B. A.; Hassellöv, M. Challenges in Exposure Modeling of Nanoparticles in Aquatic Environments. *Hum. Ecol. Risk Assess.* **2011**, *17* (1), 245–262.
- (52) Gottschalk, F.; Sonderer, T.; Scholz, R. W.; Nowack, B. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environ. Sci. Technol.* **2009**, *43* (24), 9216–9222.
- (53) Gottschalk, F.; Ort, C.; Scholz, R. W.; Nowack, B. Engineered nanomaterials in rivers – Exposure scenarios for Switzerland at high spatial and temporal resolution. *Environ. Pollut.* **2011**, *159* (12), 3439–3445.
- (54) O'Brien, N.; Cummins, E. Nano-Scale Pollutants: Fate in Irish Surface and Drinking Water Regulatory Systems. *Hum. Ecol. Risk Assess.* **2010**, *16* (4), 847–872.
- (55) Koelmans, A. A.; Nowack, B.; Wiesner, M. R. Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments. *Environ. Pollut.* **2009**, *157* (4), 1110–1116.
- (56) Boxall, A.; Chaudhry, Q.; Sinclair, C.; Jones, A.; Aitken, R.; Jefferson, B.; Watts, C. Current and future predicted environmental exposure to engineered nanoparticles; [http://hero.epa.gov/index.cfm?action=reference.details&reference\\_id=196111](http://hero.epa.gov/index.cfm?action=reference.details&reference_id=196111) (accessed July 26, 2012).
- (57) Dale, A. L.; Lowry, G. V.; Casman, E. A. Stream Dynamics and Chemical Transformations Control the Environmental Fate of Silver and Zinc Oxide Nanoparticles in a Watershed-Scale Model. *Environ. Sci. Technol.* **2015**, *49* (12), 7285–7293.
- (58) Quik, J. T. K.; Lynch, I.; Hoecke, K. V.; Miermans, C. J. H.; Schampelaere, K. A. C. D.; Janssen, C. R.; Dawson, K. A.; Stuart, M. A. C.; Meent, D. V. D. Effect of natural organic matter on cerium dioxide nanoparticles settling in model fresh water. *Chemosphere* **2010**, *81* (6), 711–715.
- (59) Quik, J. T. K.; van De Meent, D.; Koelmans, A. A. Simplifying modeling of nanoparticle aggregation–sedimentation behavior in environmental systems: A theoretical analysis. *Water Res.* **2014**, *62*, 193–201.
- (60) Quik, J. T. K.; de Klein, J. J. M.; Koelmans, A. A. Spatially explicit fate modelling of nanomaterials in natural waters. *Water Res.* **2015**, *80*, 200–208.
- (61) Markus, A. A.; Parsons, J. R.; Roex, E. W. M.; de Voogt, P.; Laane, R. W. P. M. Modelling the transport of engineered metallic nanoparticles in the river Rhine. *Water Res.* **2016**, *91*, 214–224.
- (62) Dumont, E.; Johnson, A. C.; Keller, V. D. J.; Williams, R. J. Nano silver and nano zinc-oxide in surface waters – Exposure estimation for Europe at high spatial and temporal resolution. *Environ. Pollut.* **2015**, *196*, 341–349.
- (63) Nowack, B.; Ranville, J. F.; Diamond, S.; Gallego-Urrea, J. A.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A. A.; Klaine, S. J. Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* **2012**, *31* (1), 50–59.
- (64) Coll, C.; Notter, D.; Gottschalk, F.; Sun, T.; Som, C.; Nowack, B. Probabilistic environmental risk assessment of five nanomaterials (nano-TiO<sub>2</sub>, nano-Ag, nano-ZnO, CNT, and fullerenes). *Nano-toxicology* **2016**, *10* (4), 436–444.
- (65) Quik, J. T. K.; Vonk, J. A.; Hansen, S. F.; Baun, A.; Van De Meent, D. How to assess exposure of aquatic organisms to manufactured nanoparticles? *Environ. Int.* **2011**, *37* (6), 1068–1077.
- (66) Mackay, D. *Multimedia Environmental Models: The Fugacity Approach*, Second ed.; CRC Press: Boca Raton, FL, 2001.
- (67) Mackay, D.; Arnot, J. A. The Application of Fugacity and Activity to Simulating the Environmental Fate of Organic Contaminants. *J. Chem. Eng. Data* **2011**, *56*, 1348–1355.
- (68) Thibodeaux, L. J.; Mackay, D. *Handbook of Chemical Mass Transport in the Environment*; CRC Press: Boca Raton, FL, 2010.
- (69) Warren, C.; Mackay, D.; Whelan, M.; Fox, K. Mass balance modelling of contaminants in river basins: Application of the flexible matrix approach. *Chemosphere* **2007**, *68* (7), 1232–1244.
- (70) Lowry, G. V.; Gregory, K. B.; Apte, S. C.; Lead, J. R. Transformations of nanomaterials in the environment. *Environ. Sci. Technol.* **2012**, *46* (13), 6893–6899.
- (71) Lowry, G. V.; Espinasse, B. P.; Badireddy, A. R.; Richardson, C. J.; Reinsch, B. C.; Bryant, L. D.; Bone, A. J.; Deonaraine, A.; Chae, S.; Therezien, M.; et al. Long-Term Transformation and Fate of Manufactured Ag Nanoparticles in a Simulated Large Scale Freshwater Emergent Wetland. *Environ. Sci. Technol.* **2012**, *46* (13), 7027–7036.
- (72) Dale, A.; Casman, E. A.; Lowry, G. V.; Lead, J. R.; Viparelli, E.; Baalousha, M. A. Modeling nanomaterial environmental fate in aquatic systems. *Environ. Sci. Technol.* **2015**, *49* (5), 2587–2593.
- (73) Mueller, N. C.; Nowack, B. Exposure Modeling of Engineered Nanoparticles in the Environment. *Environ. Sci. Technol.* **2008**, *42* (12), 4447–4453.
- (74) Sani-Kast, N.; Scheringer, M.; Slomberg, D.; Labille, J.; Praetorius, A.; Ollivier, P.; Hungerbühler, K. Addressing the complexity of water chemistry in environmental fate modeling for engineered nanoparticles. *Sci. Total Environ.* **2015**, *535*, 150–159.
- (75) Praetorius, A.; Tufenkji, N.; Goss, K.-U.; Scheringer, M.; von der Kammer, F.; Elimelech, M. The road to nowhere: equilibrium

- partition coefficients for nanoparticles. *Environ. Sci.: Nano* **2014**, *1* (4), 317–323.
- (76) Cornelis, G. Fate descriptors for engineered nanoparticles: the good, the bad, and the ugly. *Environ. Sci.: Nano* **2015**, *2*, 19.
- (77) Dale, A. L.; Lowry, G. V.; Casman, E. A. Much ado about  $\alpha$ : reframing the debate over appropriate fate descriptors in nanoparticle environmental risk modeling. *Environ. Sci.: Nano* **2015**, *2*, 27.
- (78) Westerhoff, P.; Nowack, B. Searching for Global Descriptors of Engineered Nanomaterial Fate and Transport in the Environment. *Acc. Chem. Res.* **2013**, *46* (3), 844–853.
- (79) USGS. Water Resources: About USGS Water Resources; <https://water.usgs.gov/GIS/huc.html> (accessed April 8, 2017).
- (80) USEPA. PCS-ICIS Customized Search: Facility Information; <https://www.epa.gov/enviro/pcs-icis-search> (accessed March 10, 2017).
- (81) Lazareva, A.; Keller, A. A. Estimating Potential Life Cycle Releases of Engineered Nanomaterials from Wastewater Treatment Plants. *ACS Sustainable Chem. Eng.* **2014**, *2* (7), 1656–1665.
- (82) Wang, H.; Adeleye, A. S.; Huang, Y.; Li, F.; Keller, A. A. Heteroaggregation of nanoparticles with biocolloids and geocolloids. *Adv. Colloid Interface Sci.* **2015**, *226* (Part A), 24–36.
- (83) Zhou, D.; Ji, Z.; Jiang, X.; Dunphy, D. R.; Brinker, J.; Keller, A. A. Influence of Material Properties on TiO<sub>2</sub> Nanoparticle Agglomeration. *PLoS One* **2013**, *8* (11), e81239.
- (84) Baalousha, M.; Kammer, F.; Motelica-Heino, M.; Le Coustumer, P. 3D characterization of natural colloids by FIFFF-MALLS-TEM. *Anal. Bioanal. Chem.* **2005**, *383* (4), 549–556.
- (85) Wigginton, N.; Haus, K.; Hochella, M., Jr. Aquatic environmental nanoparticles. *J. Environ. Monit.* **2007**, *9*, 1306–1316.
- (86) Nho-Kim, E.-Y.; Michou, M.; Peuch, V.-H. Parameterization of size-dependent particle dry deposition velocities for global modeling. *Atmos. Environ.* **2004**, *38* (13), 1933–1942.
- (87) Zhang, L.; Wang, X.; Moran, M.; Feng, J. Review and uncertainty assessment of size-resolved scavenging coefficient formulations for below-cloud snow scavenging of atmospheric aerosols. *Atmos. Chem. Phys.* **2013**, *13*, 10005–10025.
- (88) Eisenreich, S. J. Atmospheric Role in Trace Metal Exchange at the Air-Water Interface. *J. Great Lakes Res.* **1982**, *8* (2), 243–256.
- (89) Kerman, B. R. On aerosol production and enrichment by breaking wind waves. *Atmos.-Ocean* **1986**, *24* (4), 329–345.
- (90) Cipriano, R. J.; Blanchard, D. C. Bubble and aerosol spectra produced by a laboratory “breaking wave. *J. Geophys. Res.* **1981**, *86* (C9), 8085–8092.
- (91) Weisel, C.; Duce, R.; Fasching, J.; Heaton, R. Estimates of the Transport of Trace Metals from the Ocean to the Atmosphere. *J. Geophys. Res.* **1984**, *89* (D7), 11607–11618.
- (92) Piotrowicz, S. R.; Ray, B. J.; Hoffman, G. L.; Duce, R. A. Trace metal enrichment in the sea-surface microlayer. *J. Geophys. Res.* **1972**, *77* (27), 5243–5254.
- (93) Duce, R.; Hoffman, G.; Zoller, W. Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural. *Science* **1975**, *187*, 59–61.
- (94) Rahn, K. *The Chemical Composition of the Atmospheric Aerosol*; University of Rhode Island, School of Oceanography: Kingston, RI, 1975.
- (95) Langevin, S. A. The role of metals in air-water interactions in Lake Superior. MS Thesis, University of Minnesota, Minneapolis, 1978.
- (96) Gillette, D. A. Threshold friction velocities for dust production for agricultural soils. *J. Geophys. Res.* **1988**, *93* (D10), 12645–12662.
- (97) Gillette, D. A.; Adams, J.; Endo, A.; Smith, D.; Kihl, R. Threshold velocities for input of soil particles into the air by desert soils. *J. Geophys. Res.* **1980**, *85* (C10), 5621–5630.
- (98) Gillette, D. A.; Passi, R. Modeling dust emission caused by wind erosion. *J. Geophys. Res.* **1988**, *93* (D11), 14233–14242.
- (99) Kelly, R.; Drake, N.; Barr, S. *Spatial Modelling of the terrestrial environment*; Wiley: New York, 2004.
- (100) Quik, J. T. K.; Stuart, M. C.; Wouterse, M.; Peijnenburg, W.; Hendriks, A. J.; van de Meent, D. Natural colloids are the dominant factor in the sedimentation of nanoparticles. *Environ. Toxicol. Chem.* **2012**, *31* (5), 1019–1022.
- (101) Brunelli, A.; Pojana, G.; Callegaro, S.; Marcomini, A. Agglomeration and sedimentation of titanium dioxide nanoparticles (n-TiO<sub>2</sub>) in synthetic and real waters. *J. Nanopart. Res.* **2013**, *15*, 1684.
- (102) Battin, T. J.; v.d. Kammer, F.; Weilharter, A.; Ottofuelling, S.; Hofmann, T. Nanostructured TiO<sub>2</sub>: Transport Behavior and Effects on Aquatic Microbial Communities under Environmental Conditions. *Environ. Sci. Technol.* **2009**, *43* (21), 8098–8104.
- (103) Bian, S.-W.; Mudunkotuwa, I. A.; Rupasinghe, T.; Grassian, V. H. Aggregation and Dissolution of 4 nm ZnO Nanoparticles in Aqueous Environments: Influence of pH, Ionic Strength, Size, and Adsorption of Humic Acid. *Langmuir* **2011**, *27* (10), 6059–6068.
- (104) Visual MINTEQ/Visual MINTEQ – a free equilibrium speciation model; <http://vminteq.lwr.kth.se/> (accessed January 28, 2016).
- (105) David, C. A.; Galceran, J.; Rey-Castro, C.; Puy, J.; Companys, E.; Salvador, J.; Monné, J.; Wallace, R.; Vakourov, A. Dissolution Kinetics and Solubility of ZnO Nanoparticles Followed by AGNES. *J. Phys. Chem. C* **2012**, *116* (21), 11758–11767.
- (106) Bear, J. *Dynamics of Fluids In Porous Media*; American Elsevier Publishing Company: New York, 1972.
- (107) Steenhuis, T.; Winchell, M.; Rossing, J.; Zollweg, J.; Walter, M. SCS Runoff Equation Revisited for Variable-Source Runoff Areas. *J. Irrig. Drain. Eng.* **1995**, *121* (3), 234–238.
- (108) Ben-Moshe, T.; Dror, I.; Berkowitz, B. Transport of metal oxide nanoparticles in saturated porous media. *Chemosphere* **2010**, *81* (3), 387–393.
- (109) Cheng, X.; Kan, A. T.; Tomson, M. B. Study of C60 transport in porous media and the effect of sorbed C60 on naphthalene transport. *J. Mater. Res.* **2005**, *20* (12), 3244–3254.
- (110) Fang, J.; Shan, X.; Wen, B.; Lin, J.; Owens, G. Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environ. Pollut.* **2009**, *157* (4), 1101–1109.
- (111) Wang, Y.; Gao, B.; Morales, V. L.; Tian, Y.; Wu, L.; Gao, J.; Bai, W.; Yang, L. Transport of titanium dioxide nanoparticles in saturated porous media under various solution chemistry conditions. *J. Nanopart. Res.* **2012**, *14* (9), 1095.
- (112) Han, P.; Wang, X.; Cai, L.; Tong, M.; Kim, H. Transport and retention behaviors of titanium dioxide nanoparticles in iron oxide-coated quartz sand: Effects of pH, ionic strength, and humic acid. *Colloids Surf., A* **2014**, *454*, 119–127.
- (113) Cornelis, G.; Kirby, J. K.; Beak, D.; Chittleborough, D.; McLaughlin, M. J. A method for determination of retention of silver and cerium oxide manufactured nanoparticles in soils. *Environ. Chem.* **2010**, *7* (3), 298–308.
- (114) Zhao, L. J.; Peralta-Videa, J. R.; Hernandez-Viezcas, J. A.; Hong, J.; Gardea-Torresdey, J. L. Transport and Retention Behavior of ZnO Nanoparticles in Two Natural Soils: Effect of Surface Coating and Soil Composition. *J. Nano Res.* **2012**, *17*, 229–242.
- (115) Chen, G.; Liu, X.; Su, C. Distinct Effects of Humic Acid on Transport and Retention of TiO<sub>2</sub> Rutile Nanoparticles in Saturated Sand Columns. *Environ. Sci. Technol.* **2012**, *46* (13), 7142–7150.
- (116) Li, Z.; Sahle-Demessie, E.; Hassan, A. A.; Sorial, G. A. Transport and deposition of CeO<sub>2</sub> nanoparticles in water-saturated porous media. *Water Res.* **2011**, *45* (15), 4409–4418.
- (117) Petosa, A. R.; Brennan, S. J.; Rajput, F.; Tufenkji, N. Transport of two metal oxide nanoparticles in saturated granular porous media: Role of water chemistry and particle coating. *Water Res.* **2012**, *46* (4), 1273–1285.
- (118) Chowdhury, I.; Hong, Y.; Honda, R. J.; Walker, S. L. Mechanisms of TiO<sub>2</sub> nanoparticle transport in porous media: Role of solution chemistry, nanoparticle concentration, and flowrate. *J. Colloid Interface Sci.* **2011**, *360* (2), 548–555.
- (119) Jiang, X.; Wang, X.; Tong, M.; Kim, H. Initial transport and retention behaviors of ZnO nanoparticles in quartz sand porous media coated with *Escherichia coli* biofilm. *Environ. Pollut.* **2013**, *174*, 38–49.

- (120) Jones, E. H.; Su, C. Fate and transport of elemental copper (CuO) nanoparticles through saturated porous media in the presence of organic materials. *Water Res.* **2012**, *46* (7), 2445–2456.
- (121) Lecoanet, H. F.; Bottero, J.-Y.; Wiesner, M. R. Laboratory Assessment of the Mobility of Nanomaterials in Porous Media. *Environ. Sci. Technol.* **2004**, *38* (19), 5164–5169.
- (122) Vecchia, E. D.; Luna, M.; Sethi, R. Transport in Porous Media of Highly Concentrated Iron Micro- and Nanoparticles in the Presence of Xanthan Gum. *Environ. Sci. Technol.* **2009**, *43* (23), 8942–8947.
- (123) Heggelund, L. R.; Diez-Ortiz, M.; Lofts, S.; Lahive, E.; Jurkschat, K.; Wojnarowicz, J.; Cedergreen, N.; Spurgeon, D.; Svendsen, C. Soil pH effects on the comparative toxicity of dissolved zinc, non-nano and nano ZnO to the earthworm *Eisenia fetida*. *Nanotoxicology* **2014**, *8* (5), 559–572.
- (124) Rousk, J.; Ackermann, K.; Curling, S. F.; Jones, D. L. Comparative Toxicity of Nanoparticulate CuO and ZnO to Soil Bacterial Communities. *PLoS One* **2012**, *7* (3), e34197.
- (125) Dimkpa, C. O.; Latta, D. E.; McLean, J. E.; Britt, D. W.; Boyanov, M. I.; Anderson, A. J. Fate of CuO and ZnO Nano- and Microparticles in the Plant Environment. *Environ. Sci. Technol.* **2013**, *47* (9), 4734–4742.
- (126) Kool, P. L.; Ortiz, M. D.; van Gestel, C. A. M. Chronic toxicity of ZnO nanoparticles, non-nano ZnO and ZnCl<sub>2</sub> to *Folsomia candida* (Collembola) in relation to bioavailability in soil. *Environ. Pollut.* **2011**, *159* (10), 2713–2719.
- (127) Choy, C. C.; Wazne, M.; Meng, X. Application of an empirical transport model to simulate retention of nanocrystalline titanium dioxide in sand columns. *Chemosphere* **2008**, *71* (9), 1794–1801.
- (128) Lecoanet, H. F.; Wiesner, M. R. Velocity Effects on Fullerene and Oxide Nanoparticle Deposition in Porous Media. *Environ. Sci. Technol.* **2004**, *38* (16), 4377–4382.
- (129) Saleh, N.; Kim, H.-J.; Phenrat, T.; Matyjaszewski, K.; Tilton, R. D.; Lowry, G. V. Ionic Strength and Composition Affect the Mobility of Surface-Modified Fe<sub>0</sub> Nanoparticles in Water-Saturated Sand Columns. *Environ. Sci. Technol.* **2008**, *42* (9), 3349–3355.
- (130) Park, C. M.; Chu, K. H.; Heo, J.; Her, N.; Jang, M.; Son, A.; Yoon, Y. Environmental behavior of engineered nanomaterials in porous media: a review. *J. Hazard. Mater.* **2016**, *309*, 133–150.
- (131) Garner, K. L.; Suh, S.; Lenihan, H. S.; Keller, A. A. Species Sensitivity Distributions for Engineered Nanomaterials. *Environ. Sci. Technol.* **2015**, *49* (9), 5753–5759.
- (132) Gottschalk, F.; Kost, E.; Nowack, B. Engineered nanomaterials in water and soils: a risk quantification based on probabilistic exposure and effect modeling. *Environ. Toxicol. Chem.* **2013**, *32* (6), 1278–1287.
- (133) Collin, B.; Auffan, M.; Johnson, A. C.; Kaur, I.; Keller, A. A.; Lazareva, A.; Lead, J. R.; Ma, X.; Merrifield, R. C.; Svendsen, C.; et al. Environmental release, fate and ecotoxicological effects of manufactured ceria nanomaterials. *Environ. Sci.: Nano* **2014**, *1*, 533–548.
- (134) Adam, N.; Vakurov, A.; Knapen, D.; Blust, R. The chronic toxicity of CuO nanoparticles and copper salt to *Daphnia magna*. *J. Hazard. Mater.* **2015**, *283*, 416–422.
- (135) Ma, R.; Levard, C.; Judy, J. D.; Unrine, J. M.; Durenkamp, M.; Martin, B.; Jefferson, B.; Lowry, G. V. Fate of Zinc Oxide and Silver Nanoparticles in a Pilot Wastewater Treatment Plant and in Processed Biosolids. *Environ. Sci. Technol.* **2014**, *48* (1), 104–112.
- (136) Musee, N.; Zvimba, J. N.; Schaefer, L. M.; Nota, N.; Sikhwihilu, L. M.; Thwala, M. Fate and behavior of ZnO- and Ag-engineered nanoparticles and a bacterial viability assessment in a simulated wastewater treatment plant. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2014**, *49* (1), 59–66.
- (137) Hou, L.; Xia, J.; Li, K.; Chen, J.; Wu, X.; Li, X. Removal of ZnO nanoparticles in simulated wastewater treatment processes and its effects on COD and NH<sub>4</sub><sup>+</sup>-N reduction. *Water Sci. Technol.* **2012**, *67* (2), 254–260.
- (138) Chaúque, E. F. C.; Zvimba, J. N.; Ngila, J. C.; Musee, N. Stability studies of commercial ZnO engineered nanoparticles in domestic wastewater. *Phys. Chem. Earth Parts ABC* **2014**, *67–69*, 140–144.
- (139) Baek, Y.-W.; An, Y.-J. Microbial toxicity of metal oxide nanoparticles (CuO, NiO, ZnO, and Sb<sub>2</sub>O<sub>3</sub>) to *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus aureus*. *Sci. Total Environ.* **2011**, *409* (8), 1603–1608.
- (140) Bradford, G.; Change, A.; Page, A.; Bakhtar, D.; Frampton, J.; Wright, H. *Background Concentrations of Trace and Major Elements in California Soils*; University of California: Riverside, 1996.
- (141) McLaughlin, M. J.; Smolders, M. J. Background zinc concentrations in soil affect the zinc sensitivity of soil microbial processes—a rationale for a metalloregion approach to risk assessments. *Environ. Toxicol. Chem.* **2001**, *20* (11), 2639–2643.
- (142) Nel, A.; Xia, T.; Meng, H.; Wang, X.; Lin, S.; Ji, Z.; Zhang, H. Nanomaterial Toxicity Testing in the 21st Century: Use of a Predictive Toxicological Approach and High-Throughput Screening. *Acc. Chem. Res.* **2013**, *46* (3), 607–621.
- (143) Li, N.; Georas, S.; Alexis, N.; Fritz, P.; Xia, T.; Williams, M. A.; Horner, E.; Nel, A. Why Ambient Ultrafine and Engineered Nanoparticles Should Receive Special Attention for Possible Adverse Health Outcomes in Humans. *J. Allergy Clin. Immunol.* **2016**, *138* (2), 386–396.
- (144) Gottschalk, F.; Scholz, R. W.; Nowack, B. Probabilistic material flow modeling for assessing the environmental exposure to compounds: Methodology and an application to engineered nano-TiO<sub>2</sub> particles. *Environ. Model. Softw.* **2010**, *25* (3), 320–332.