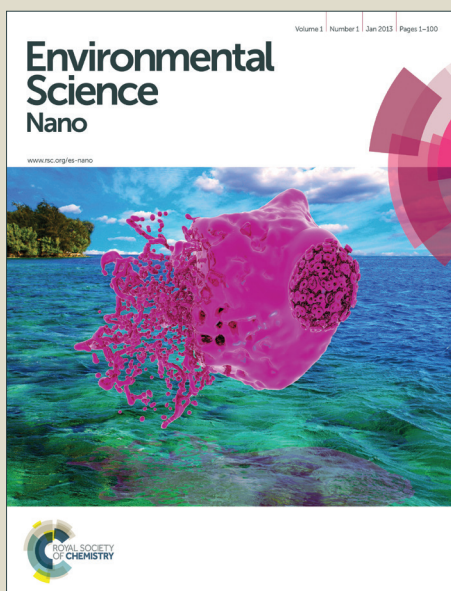


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Nano Impact Statement:

A recent Perspective in this journal (Praetorius et al., 2014) favors engineered nanoparticle (ENP) fate models based on colloid science (particle balance) over mass-based alternatives because the latter often incorrectly assume that contaminant distribution between solid phases and water is at equilibrium. We show that mass-based models need not assume equilibrium. Further, we show they can be as effective as particle balance for risk assessment at large scales even when they apply simple heuristics. This paper broadens the current debate over appropriate fate descriptors for ENPs and cautions against the premature censure of alternative modeling approaches until understanding of ENP heteroaggregation improves, model validation can be performed, and model error can be systematically evaluated and compared across alternative frameworks.

Much ado about α : Reframing the debate over appropriate fate descriptors in nanoparticle environmental risk modeling

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Abstract

Large-scale fate and transport models have used different approaches to account for engineered nanoparticle (ENP) heteroaggregation and its effects on fate. Praetorius et al. and Cornelis, in recent *Perspectives* in this journal, favor the use of particle number-based kinetic models and attachment efficiency, α , in place of mass-based approaches relying on partition coefficients, or K_d values, because the former is more theoretically faithful to the particulate nature of ENPs. Here, we provide perspective on these two popular modeling frameworks, particle balance and mass balance, with regards to their ability to capture ENP fate processes at large scales. We show that particle balance using α is not unique in its ability to describe ENP heteroaggregation kinetically, since mathematically equivalent rates can be created for mass balance, and that the ability of particle balance to accurately describe particle behaviors is still severely hindered by evolving scientific understanding of ENP heteroaggregation. Ultimately, we find that models at this scale are relatively insensitive to the particulate nature of ENPs. In the short term, mass-based models that rely on simple heuristics can be more practical, and less error-prone, than particle balance alternatives using α .



Abstract Art:

Abstract Art Text: Mass balance is currently as useful as number balance in nanoparticle risk assessment, even though it ignores particle properties.

Introduction

Large-scale (e.g., watershed, regional, national, and global) models have been used for decades to study the environmental fate and transport of ionic and molecular contaminants.¹ Many such models have been adapted for use with, or specifically developed for, engineered nanoparticles (ENPs),²⁻¹⁵ but recently a debate has surfaced over the best modeling approach for ENP heteroaggregation, or the attachment of ENPs to naturally-occurring solids such as soil particles or suspended sediments.^{16,17} Indeed, heteroaggregation strongly influences ENP bioavailability and mobility in the environment,¹⁷ and accounting for it in environmental models is essential to their usefulness as a scientific or decision-making tool. However, relatively little attention has been paid thus far to practical considerations affecting model selection, such as data limitations, model scale, and study objectives.

Cerco (2003) distinguished between "scientific" and "engineering" models, where scientific models are designed to enhance scientific understanding of processes and guide research efforts, and engineering models are designed with an application in mind--often to facilitate "real-time" decision-making by regulators and risk managers. He remarked that, "scientific models, as a class, tend to be limited in scope. They tend to examine at most a few processes on a local spatial scale. Engineering models, on the other hand, are usually system wide and attempt to incorporate transport, chemical, and biological processes."¹⁸ Scientific models are typically mechanistic, whereas engineering models often rely on empirical relations. Most large-scale ENP fate and transport models developed to date are engineering models (e.g., refs²⁻¹⁵).

Mechanistic heteroaggregation models based on DLVO theory and coagulation theory have recently been simplified for inclusion in the type of large-scale engineering models intended for decision-making.^{14,15} In their recent *Perspective* in this journal, Praetorius et al. argue that this is the most appropriate approach because it explicitly accounts for the colloidal nature of ENPs, unlike the mass-based alternatives developed for ionic and molecular contaminants. We examine this claim in light of ongoing practical challenges in model formulation, parameterization, and calibration for ENPs.

Mass balance and population balance in ENP fate models

Most early successes in ENP fate modeling were achieved with the mass balance framework developed to describe molecular contaminants, in which the inflow and outflow of total contaminant mass is balanced over time or at steady state (e.g., refs^{1,3-6,8-13}). Partition coefficients, or K_d values, are commonly used in mass balance to describe the solid-water distribution of contaminants. K_d (L/kg) is experimentally derived from C_s/C_{aq} , where C_s is the sorbed mass concentration (mg/kg) and C_{aq} is the aqueous mass

concentration (mg/L).¹⁹ Using K_d in a model implies that sorption is reversible and occurs so quickly relative to other processes that its time dependence can be safely ignored. In fact, a rigorous theoretical derivation of K_d requires that equilibrium has been achieved locally.^{1,20}

Recent *Perspectives* argued that, since colloidal suspensions never reach an equilibrium state, kinetic models based on colloid transport theory ("coagulation models") are a better alternative than K_d for ENPs.^{16,17} The authors describe the decrease in the number concentration of unaggregated particles over time (dN_{NP}/dt) as the product of the collision frequency, K , the attachment efficiency, α , and the number concentrations of the colliding species, N_{NP} (nanoparticles) and N_{NC} (natural colloids)²¹:

$$\frac{dN_{NP}}{dt} = -\alpha K N_{NP} N_{NC} \quad (1)$$

Terms for advection, settling, reaction, and so on are added to Equation 1 to provide a complete description of ENP fate. This framework typifies particle balance (a type of population balance), which splits a population of particles into discrete bins based on (e.g.) geochemical identity, size, and heteroaggregation state and then performs a balance on the number concentration in each bin at each model time step.²² For example, aggregation of ENPs in size class i to natural colloids in size class j is expressed as a loss in the number concentration of unaggregated ENPs and a gain in the number concentration of the size class combination (i,j) .¹⁵

Particle balance has been successfully applied in a large-scale engineering ENP fate model that includes heteroaggregation.¹⁵ It has not yet been applied to a dynamic system or to systems with reactive ENPs. In support of this approach, there has been a recent spike in the publication of empirically-determined α 's or related parameters (e.g., Debye length) for use in such models.^{21, 23, 24}

The two approaches are not entirely interchangeable. Error can arise when converting number concentrations to mass concentrations because particle balance models discretize mass by discretizing size. Similarly, mass concentrations cannot be converted to number concentrations unless the size distribution is known or estimated. Conversion between mass and number concentrations is most error-prone when the nanoparticle sizes are changing over time. For example, numerical dispersion can occur when modeling highly reactive particles using particle balance. To avoid these errors, some coagulation models balance both mass and particle number.²⁵

The most important difference between particle balance and mass balance is not what they balance, but rather their approach to scale-up. Mass balance tends to simplify. For example, K_d allows modelers to express free and solid-associated mass concentrations using a single state variable. In particle balance, each particle and heteroaggregate size and type is assigned its own state variable. Particle

balance typically uses binning to scale up process-based descriptions of individual particle behaviors (collisions, surface area-dependent reactions) to the entire population. Mass balance typically neglects differences between ENPs in the population, averaging them through the choice of parameters. This approach implies differences are irrelevant at the scale of interest to the modeler.

Challenges in population balance modeling of ENPs

Of the two approaches, population balance is more faithful to nanoparticle-specific properties and processes. However, this strength for scientific models can be a weakness in large-scale engineering models.

Because of the need to assign a separate continuity equation to each particle type and size, computational burden is an oft-cited weakness of particle balance at large scales,^{22,26} Certainly, it is more computational demanding than mass balance. However, analytical solutions to the coagulation equation do exist for simplified systems, including monodisperse primary particles heteroaggregating with a constant collision rate, K ,²² and steady-state solutions assuming pseudo-first-order heteroaggregation (i.e., that N_{NC} in Eq. 1 is constant).¹⁵ Since the publication of the coagulation equation in 1917, several iterative and noniterative numerical solutions have also been developed. Thus computational complexity need not be limiting; a typical atmospheric model using this approach can contain as many as 10^4 state variables solved for each of 10^5 grid cells.²⁵

Model parameterization is more problematic. Many α 's are needed to describe the diversity of ENPs and natural colloids in the environment (e.g., inorganic and organic particles with highly variable compositions and sizes, bacteria, algae, and macromolecules), the effects of engineered surface coatings, the complex interactions of ENPs with organic matter, and solution chemistry including ionic strength.^{14, 22, 26} Because error results from both uncertainty in model structure and in model parameters, increasing a model's faithfulness to process (beyond a certain point) can actually decrease performance by increasing the number of uncertain parameters.^{27, 28} Additionally, models with a large number of parameters (especially those that are highly correlated) often suffer from overparameterization. Such models will perform well during calibration but exhibit poor predictive performance.¹

Simplifying assumptions are thus necessary to reduce model error and complexity, especially in light of the scientific uncertainty surrounding ENP heteroaggregation.^{13-15, 22, 26} However, the scientific

validity of particle balance, or at least its superiority over mass balance, is undermined at present by its reliance on the following common assumptions: (1) unaggregated NPs and NCs are monodisperse, (2) all but one "typical" NC type can be ignored, (3) NC concentrations do not vary over time (pseudo-first-order kinetics apply), (4) the collision rate is constant and collisions are rectilinear (i.e., particles and heteroaggregates do not affect the flow field as they approach one another), (5) heteroaggregation events other than single NP/single NC collisions can be ignored (where the NC can represent a homoaggregate of primary NCs but higher-order NC/NC collisions are not considered), (6) variation in α due to the effects organic matter, engineered surface coatings, and solution chemistry can be ignored, and (8) no aggregate break-up is considered. With respect to the last assumption, neither complete reversibility of aggregation (assumed for K_d) nor complete irreversibility (assumed for α) are likely to occur in natural environments. Break-up has been repeatedly observed in soil systems for colloids such as bacteria and viruses, and is often accounted for in such models by assuming the presence of a non-sorbing fraction.²⁹

Finally, some methodological problems with α should be noted. Theoretical determinations of α (via classic and extended DLVO theory) have consistently failed to show quantitative or even qualitative agreement with experimental results,³⁰⁻³⁴ so α must (like K_d) be determined empirically.^{17,26} Although the experimental setup for determining α (column studies) is less operationally defined than that of K_d (batch studies), significant differences do still remain between column studies and the natural environment.¹⁷ For example, comparisons of field-scale studies to column studies on the mobility of bacteria, protozoa, and viruses suggest that estimates of α for these colloidal organisms decrease as the scale of the study increases.²⁹

The case for mass balance

Because mass balance models do not track the particle size distribution over time, they are generally unable to describe size-dependent processes that may affect ENP behavior, e.g. the reaction rate increases that occur as ENPs dissolve. However, these effects can be minor and large-scale models may not be sensitive to these differences. Reactive ENP dissolution rates and solubilities vary less than an order of magnitude for silver ENPs of different sizes (4 vs. 60 nm)³⁵ and ZnO NPs (4 vs. 241 nm),³⁶ and several studies suggest size may play a relatively minor role in ENP speciation and toxicity, especially when compared to environmental factors such as pH, soil type, and redox conditions.³⁶⁻³⁸ Figure 1 compares a mass-based shrinking particle model³⁹ of the dissolution of spherical silver ENPs to an alternative which assumes a size-independent reaction rate¹⁹ (in the standard units of d^{-1}) at three temperatures. Particle shrinkage has a relatively small effect compared to temperature. Note that this model assumes the dissolution rate increases proportionately to the increase in specific surface area. Non-proportional rate

behavior is theoretically possible for ENPs but has not been reported in kinetic studies of silver NP dissolution.^{35, 40, 41}

K_d values are not strictly appropriate for ENPs because the equilibrium assumption is invalid for colloidal suspensions.^{16, 17} However, in spite of this, partition coefficients and their operationally-defined, experimentally determined counterparts, retention coefficients (K_r),¹⁷ have long been used as screening-level heuristic for species that do not follow the equilibrium assumption such as metal ions.^{20, 42} Ramaswami et al. state "equilibrium conditions are often not attained in the environment ... However, equilibrium calculations are relatively straightforward to make and provide a good first estimate of the overall distribution of a chemical in the different media ... (72)"¹

Of course, rather than relying on the equilibrium assumption, kinetic rates of formation and break-up of heteroaggregates of different sizes or types can also easily be incorporated into mass balance. Consider Equation 2, a mass-based analog to Equation 1 where the product of α and K is replaced with a second-order (mass-based) rate of heteroaggregation, $k_{het,mass}$:

$$\frac{dC_{NP}}{dt} = -k_{het,mass} C_{NP} C_{NC} \quad (2)$$

Unlike K_d , this formulation requires at least two state variables, one for the unaggregated NPs and one for the aggregates. However, it is still simple to implement and can be made pseudo-first-order if C_{NC} is constant. Limousin et al. (2007) reviewed sixteen equilibrium approaches and eight kinetic approaches to sorption developed for mass balance modeling of "conventional" (non-nano) contaminants. They note that partition coefficients are the simplest of all available approaches.⁴³

The kinetic mass-based approach that uses one state variable to represent unaggregated NPs and another to represent aggregates is in fact equivalent to a population balance approach in which only a single size class is considered for each particle type and aggregation events other than those between single NPs and single NCs are ignored. More complex formulations, such as multiple size classes, also have direct analogs. In fact, the interchangeability of kinetic mass-based models and particle number balance models reduced for use at large scales (minus some conversion error, discussed previously) has already been noted and applied for ENPs.^{13, 26} Quik et al. (2014) showed that the population balance model for aggregation and sedimentation can be reliably replaced with a mass balance equivalent that follows a first-order loss rate to a non-sorbing fraction.²⁶

The choice of simulation method for ENP heteroaggregation will only be relevant if the model under consideration is sensitive to that choice with respect to the output of interest. Using a "complete removal" case for surface water segments as compared to a "no removal" case resulted in only a factor of

three difference between predicted median surface water concentrations (0.43 $\mu\text{g/L}$ versus 0.14) of nano- TiO_2 in a spatially resolved model of Swiss rivers.⁸ Out of seven tested parameters, Blaser et al. (2008) found that their model was less sensitive to K_d than to two other parameters in the water column (water velocity and the settling velocity of solids) and five others in the sediment.³ In contrast, Liu and Cohen find that the percent removal of ENPs from the water column by sedimentation as opposed to outflow will increase rapidly (from 0 to ~40%) for "attachment factors" above approximately 0.95.¹² This fate descriptor equals $C_s/(C_s + C_{aq})$ and corresponds to a K_d of 19, which is small compared to K_d values reported for some NPs but may be realistic for others (K_d or $K_r = 0.9$ to 250 for C_{60} ;^{44, 45} 590 (median)⁴⁶ and 30,000 (mean)⁴⁷ for Ag NPs; 9.2 (median) for CeO_2 NPs⁴⁸). Praetorius et al. (2012) found relatively small differences in ENP mobility between an $\alpha=0.1$ and $\alpha=1.0$ case, although more significant differences were observed for $\alpha < 0.1$.¹⁵ Therezien et al. (2014) showed that complete heteroaggregation occurs in at most several weeks in a box model of nanosilver and NC homo- and heteroaggregation under a wide range of conditions (20 nm or 100 nm silver NPs, NC diameters prior to aggregation between 50 and 2000 nm, background NC concentrations between 0 and 100 mg/L, and α 's between 0.005 and 1). The half-life of a dose of 0.25 ppm unaggregated NPs is less than a day when $\alpha > 0.05$ and the background NC concentration is above ~15 mg/L, which seems likely in natural systems.²²

Rapid aggregation and settling of ENPs has been observed in quiescent⁴⁹ and turbulent⁵⁰ experimental systems. Equation 1 reveals that even low α 's can result in high attachment when K is high (e.g., when colloids are abundant). In systems with long residence times (> 1 day) and those in which ENPs heteroaggregate prior to entering the system, even the simple assumption of 100% ENP association with the solid phase should yield results similar to that of a particle balance model assuming irreversible heteroaggregation.

Ultimately, at large scales, model error arising from ignoring nanoparticle-specific properties is likely to be overshadowed by variation in model output due to either uncertainty or natural variation in other input parameters or process descriptions, such as ENM production estimates and the speciation of ENPs within sewage treatment plants and biosolids.¹¹

No matter which framework is employed, one important consideration is how best to subdivide the solid phase in order to ensure that mobile fractions are distinguished from immobile fractions and high-sorbing fractions are distinguished from low-sorbing fractions at the level of detail appropriate to the analysis. For example, many models designed to capture sediment movement in rivers and river beds (e.g., surface runoff, bank erosion, settling, resuspension, bed load shift, and burial) as a function of time-variable stream flow break sediment into size classes (e.g., clay, sand, and silt) with diameter-dependent parameter values.⁵¹

Conclusion

Scientific models are testable mathematical hypotheses of how a phenomenon works, usually under simple and controlled conditions. Engineering models, in contrast, are designed to describe the essential features of a phenomenon at large-scales for decision-making purposes. There is no question that α is the appropriate fate descriptor for small-scale scientific models, but this is not necessarily the case for large-scale engineering models, which must abstract greatly from first principles and thus cannot be judged solely on the theoretical purity of their assumptions. As Dominic DiToro noted, engineering models must compromise between simplicity and realism. "The best solution emphasizes the former without undue violence to the latter."⁵² Particle balance models for ENPs are more complex and difficult to parameterize, and at present they do not appear to add appreciably to the realism of large-scale EMN fate models. Concerns about the equilibrium assumption behind K_d can be easily put to rest by developing mass balance models that rely instead on overall rates of sorption and desorption. However, these models ultimately appear relatively insensitive to the choice of ENP heteroaggregation fate descriptor, and simple approaches such as assuming 100% sorption of ENPs to a solid phase may be appropriate for engineering models of most systems, at least until scientific understanding of ENP heteroaggregation substantially improves.

Because the ultimate test of an engineering model is its ability to match and predict experimental observations during calibration or validation, and because challenges in detecting and characterizing ENPs in environmental matrices are significant and ongoing,⁵³ neither mass-based nor population-based frameworks can yet be decisively shown to be better than the other. However, we can perform sensitivity analyses to determine whether the particulate nature of ENPs strongly influences their environmental fate. For example, Fig. 1 shows that the dissolution rate of an aqueous suspension of pristine silver nanoparticles is more sensitive to temperature than to particle shrinkage. While, with increasing computational power and improving environmental measurement capabilities, process-based scientific models and "big picture" engineering models may someday converge, they presently occupy valid, but distinct, practical niches. In the short term, the desire for theoretical purity should not outweigh the practical utility of mass balance for risk assessment purposes.

Figures

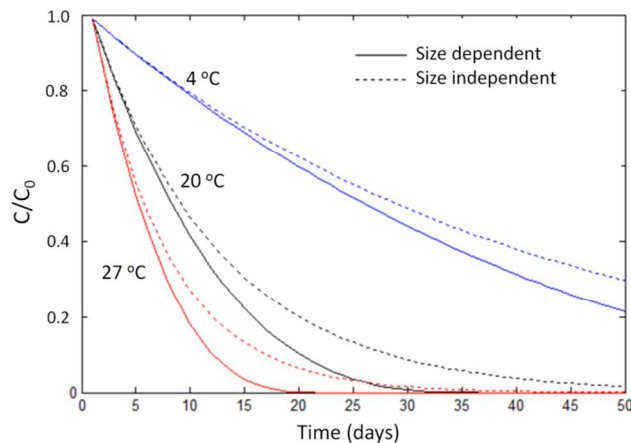


Fig. 1. A simple box model of the dissolution of a monodisperse solution of unsulfidized silver ENPs predicts relatively little error results from an assumption that "per day" mass-based reaction rates remain constant as the particle shrinks when compared to the effect of temperature (assuming an Arrhenius temperature coefficient of 1.08).

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