

 Open access • Journal Article • DOI:10.1007/S11051-014-2503-2

Emerging patterns for engineered nanomaterials in the environment: a review of fate and toxicity studies — [Source link](#)

Kendra L. Garner, Arturo A. Keller

Institutions: University of California, Santa Barbara, University of California

Published on: 03 Jul 2014 - Journal of Nanoparticle Research (Springer Netherlands)

Related papers:

- [Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local](#)
- [Global life cycle releases of engineered nanomaterials](#)
- [Modeled Environmental Concentrations of Engineered Nanomaterials \(TiO₂, ZnO, Ag, CNT, Fullerenes\) for Different Regions](#)
- [Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions.](#)
- [Transformations of nanomaterials in the environment.](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/emerging-patterns-for-engineered-nanomaterials-in-the-364cvhq7mt>

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Emerging patterns for engineered nanomaterials in the environment: A review of fate and toxicity studies

Permalink

<https://escholarship.org/uc/item/0fg3t37g>

Journal

Journal of Nanoparticle Research, 16(8)

ISSN

1388-0764

Authors

Garner, KL
Keller, AA

Publication Date

2014

DOI

10.1007/s11051-014-2503-2

Peer reviewed

Emerging patterns for engineered nanomaterials in the environment: a review of fate and toxicity studies

Kendra L. Garner · Arturo A. Keller

Received: 31 March 2014 / Accepted: 5 June 2014 / Published online: 3 July 2014
© Springer Science+Business Media Dordrecht 2014

Abstract A comprehensive assessment of the environmental risks posed by engineered nanomaterials (ENMs) entering the environment is necessary, due in part to the recent predictions of ENM release quantities and because ENMs have been identified in waste leachate. The technical complexity of measuring ENM fate and transport processes in all environments necessitates identifying trends in ENM processes. Emerging information on the environmental fate and toxicity of many ENMs was collected to provide a better understanding of their environmental implications. Little research has been conducted on the fate of ENMs in the atmosphere; however, most studies indicate that ENMs will in general have limited transport in the atmosphere due to rapid settling. Studies of ENM fate in realistic aquatic media indicates that in general, ENMs are more stable in freshwater and stormwater than in seawater or groundwater, suggesting that transport may be higher in freshwater than in seawater. ENMs in saline waters generally sediment out over the course of hours to days,

leading to likely accumulation in sediments. Dissolution is significant for specific ENMs (e.g., Ag, ZnO, copper ENMs, nano zero-valent iron), which can result in their transformation from nanoparticles to ions, but the metal ions pose their own toxicity concerns. In soil, the fate of ENMs is strongly dependent on the size of the ENM aggregates, groundwater chemistry, as well as the pore size and soil particle size. Most groundwater studies have focused on unfavorable deposition conditions, but that is unlikely to be the case in many natural groundwaters with significant ionic strength due to hardness or salinity. While much still needs to be better understood, emerging patterns with regards to ENM fate, transport, and exposure combined with emerging information on toxicity indicate that risk is low for most ENMs, though current exposure estimates compared with current data on toxicity indicates that at current production and release levels, exposure to Ag, nZVI, and ZnO may cause toxicity to freshwater and marine species.

Keywords Aggregation · Sedimentation · Dissolution · Groundwater · Soil · Natural waters · Environmental and health effects

Electronic supplementary material The online version of this article (doi:10.1007/s11051-014-2503-2) contains supplementary material, which is available to authorized users.

K. L. Garner · A. A. Keller (✉)
UC Center on the Environmental Implications of
Nanotechnology and School of Environmental Science
and Management, University of California, Santa Barbara,
CA 93106
e-mail: keller@bren.ucsb.edu

Introduction

Until a few years ago, little was known about the fate of nanomaterials in the environment, but recent studies

suggest important emerging patterns. There are still major strategic knowledge gaps for even the most widely used nanoparticles (NPs) involving their post-production life cycles, including entry into the environment, environmental pathways, eventual environmental fate, and potential ecotoxicological effects. Actual environmental concentrations of engineered nanomaterials (ENMs) are largely unknown (Peralta-Videa et al. 2011), though recent release estimates have been completed (Gottschalk et al. 2009; Hendren et al. 2013; Keller et al. 2013; Tovar-Sánchez et al. 2013) and there is emerging evidence that manufactured NPs (<100 nm), including TiO₂, are present in wastewater (Kiser et al. 2009; Westerhoff et al. 2011) and waste leachate (Hennebert et al. 2013).

By most definitions, ENMs encompass NPs synthesized and modified to enhance their performance for technical or industrial purposes that have at least one dimension less than 100 nm. They are increasingly used in a variety of consumer products including electronics, textiles, cosmetics, medicine, and food (Peralta-Videa et al. 2011). ENMs are released into the environment; either during their use, by spillages, by intentional release for environmental remediation applications, or as end-of-life waste (Keller et al. 2013). Studies estimate that more than 1,300 products that are on the market today contain NPs (Bondarenko et al. 2013) and production estimates of major ENMs range from 270,000 to 320,000 metric tons per year, of which high end estimates suggest that 17 % may be release to soils, 21 % to water, and 2.5 % to air, with the balance entering landfills (Keller and Lazareva 2013). Thus understanding the environmental and health risks associated with ENMs is of great importance. The fact that some ENMs are known to be toxic emphasizes the need for a comprehensive assessment of the environmental risks of the large quantities of ENMs entering our environment (French et al. 2009).

Once released, ENMs will interact with the environment in several ways. These interactions are controlled by the inherent properties of the ENMs (solubility in water, colloidal stability, reactivity, etc.) and the properties of the environment into which they are released (temperature, flows of air, water, and solids, and the physicochemical characteristics of each phase) (Mackay et al. 1992). Properties such as ionic strength (IS), pH, the presence of organic matter, and compartment composition are all important parameters that will modify ENM behavior (Keller et al.

2010; Lowry et al. 2012a, b; Zhou et al. 2012b). It is important to understand both how ENMs interact with their environment and how their environment alters the expected interactions.

The objective of this review is to identify the emerging trends in fate and toxicity of ENMs under various environmental conditions, as a preliminary step in understanding their environmental implications and potential risks. Since it is virtually impossible to conduct a full battery of tests that adequately describes interactions of each ENM in every environmental compartment and biological system (Johnston et al. 2010), the focus must be on identifying patterns in data that allow us to simplify our understanding of the complex interactions among ENMs and abiotic and biotic compartments across a range of conditions (Johnston et al. 2010). This review of the literature on fate and toxicity of ENMs in air, water, and soil showed that patterns are emerging that allow us to characterize rates of aggregation, sedimentation, dissolution, and toxicity in various aquatic media including stormwater, freshwater, groundwater, and seawater. The current status of the literature does not allow us to draw the same level of conclusions for air and soil; though an initial attempt is made to understand basic patterns in how ENMs interact with these media. By comparing fate and transport patterns with potential environmental release concentrations and toxicity data, we assess which ENMs are of greatest concern.

ENM fate and transport

There are many fate and transport processes that need to be considered to understand ENM mobility, bioavailability, and ultimate fate (Fig. 1). These include ENM emissions to air, water, and soil; advection in and out of the system; diffusive transport; volatilization to air; transformation into other ENMs or compounds; aggregation; sedimentation; dissolution; filtration; and sorption to suspended particles and the subsequent deposition to sediment (Quik et al. 2011).

Many processes are important to ENMs that may not be relevant to the environmental behavior of traditional contaminants (Quik et al. 2011), such as aggregation, dissolution, deposition, and attachment. These are all determined by their size, surface

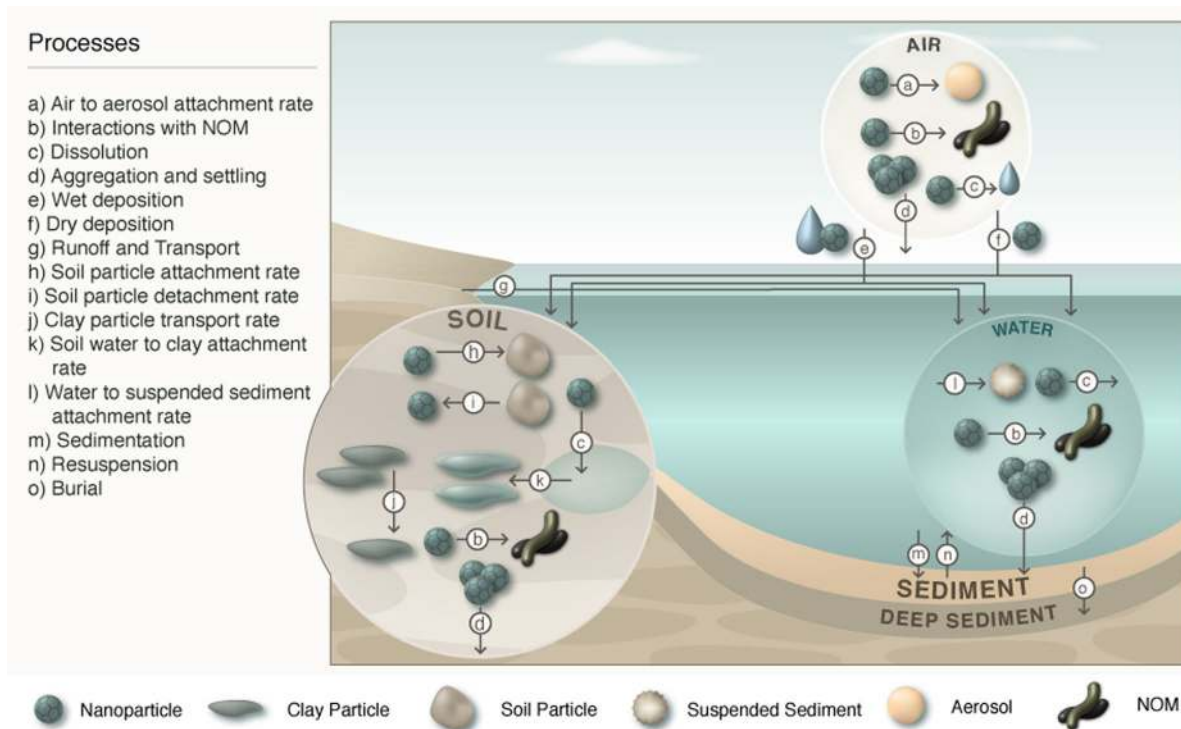


Fig. 1 Conceptual model of key ENM fate processes. Diagram by Anastasiya Lazareva. This shows how nanoparticles are transported between environmental compartments and how they may interact with other constituents in the environment as well as with themselves

properties, and ambient environmental characteristics. Further, some ENMs dissolve over time, so exposure can consist of both the suspended NPs and the dissolved ions (Stebounova et al. 2011). Some transformation processes, such as aggregation, can also create an altered state where the NP behaves in unexpected ways (Praetorius et al. 2012). For example, NP agglomerates will interact with the environment in different ways and at different rates compared with individual NPs or dissolved ions (Zhang et al. 2008). Most ENMs will also undergo transformation processes (e.g., oxidation, sulfidation) that alter their original properties such as acquiring coatings that alter their chemical properties and environmental behavior (Lowry et al. 2012a, b; Praetorius et al. 2012). In attempting to identify patterns in the fate and transformation processes, complicating factors such as uncertainties regarding NP emissions into the environment, ENM coatings, interactions with natural colloids and natural organic matter (NOM), and the effect of ambient environmental properties, limit the extent to which we can make broad conclusions about

ENM fate and transport patterns (Arvidsson et al. 2011).

Fate and transport in air

ENMs are emitted to the atmosphere through either indirect or diffuse sources (Gottschalk et al. 2011) and will eventually deposit to land and surface waters. Recent studies indicate that ENM release to the atmosphere is quite small, with a high end estimate of 8,300 metric tons released annually around the globe (Keller and Lazareva 2013). While this may be quite small relative to other releases, and the residence time in the atmosphere is likely quite short, atmospheric fate and transport should not be disregarded. It is likely that localized releases of ENMs, such as from the use of aerosolized pesticides, could result in temporarily high concentrations of ENMs in the atmosphere and we need to understand both their residence time in the atmosphere and their eventual fate. While in the atmosphere, ENMs will be subject to physical and chemical alteration processes that will

modify their fate and environmental concentrations in other compartments (Tiwari and Marr 2010).

A major drawback to the current state of the art measurement devices is their lack of differentiation of background particles from ENMs (Kuhlbusch et al. 2011). Aerosol mass spectrometer is currently the only instrument capable of sizing and chemically analyzing nano-scale particles; it currently cannot measure metal and metal oxides, though this is in development (Kuhlbusch et al. 2011). Additionally, the currently available measurement devices are able to discriminate particles according to size, but not according to density (Brouwer et al. 2009). As such, current research does not provide enough data to identify significant patterns in fate and transport processes within the air compartment, indicating that additional research is needed.

When released to the atmosphere, the size of NPs and their aggregates will increase due to the condensation of organic and inorganic vapors on the particle nuclei as a result of condensation/evaporation and dilution, with some contribution from coagulation and deposition (Meesters et al. 2013; Tiwari and Marr 2010; Zhang and Wexler 2004). In condensation, semivolatile substances or water condense on a particle, forming a shell around it; whereas coagulation is the process in which particles move by Brownian motion, collide with each other, aggregate, grow in size, and decline in number (Kumar et al. 2011; Meesters et al. 2013; Tiwari and Marr 2010). Condensation may also affect fate wherein the presence of hydrophilic compounds result in enhanced aqueous solubility and mobility through porous media (Meesters et al. 2013; Tiwari and Marr 2010). Environmental factors, such as temperature, relative humidity, and atmospheric turbulence, will affect the size and concentration of ENMs in the atmosphere (Navarro et al. 2008). Additionally, ENMs will experience atmospheric degradation through oxidation and photolysis; though the extent to which these may occur is unknown (Tiwari and Marr 2010).

Little is known about the rates of aggregation and deposition of specific ENMs in the atmosphere, due largely to the complex nature of the system and the lack of instrumentation for measuring ENMs at such small sizes and concentrations. However, one study suggests that if we assume a 10 day retention time for NPs in the lower atmosphere, approximately 1/36th of the ENM input to the air compartment constantly

remains in the lower atmosphere (Gottschalk et al. 2010). This indicates that a majority of ENMs will likely settle very quickly, even given their small size. Another early study indicates that NP agglomerates are likely to remain below 1 μm which may indicate very long term persistence (Baumgartner and Loeffler 1986). Transport within the atmosphere will likely be limited as concentrations in the atmosphere are predicted to be low because most nanomaterials do not volatilize and aggregation and sedimentation will be relatively rapid (Quik et al. 2011).

A number of studies have been conducted on the fate of ENMs in the workplace (Bello et al. 2009; Curwin and Bertke 2011; Fujitani et al. 2008; Lee et al. 2012; Schneider and Jensen 2009; Seipenbusch et al. 2008; Tsai et al. 2009). These typically consider the release of ENMs to indoor air during the production of engineered nanoparticles (ENPs) or products that contain ENPs. While these studies may not fully translate to the fate of ENMs in the atmosphere, they help to elucidate processes and rates. The release of nano-sized particles at relatively low concentrations will result in bi-modal size distributions in air with one mode in the nanometer range and the other in the micrometer range; though the modes varied substantially (Brouwer 2010; Fujitani et al. 2008; Schneider and Jensen 2009; Tsai et al. 2009). Bello et al. (2009) found that the particle number concentrations for ENMs between 10 nm and 1 μm were quite stable over multiple time periods. The larger mode indicates that a majority of the atmospheric exposure will be of larger agglomerates (Brouwer 2010). Confirming this is a review by Curwin and Bertke (2011) who conducted exposure assessments for facilities producing metal oxides including titanium, magnesium, yttrium, aluminum, calcium, and iron and found that a majority of the particles in the workplace air were agglomerated with the predominant particle size between 0.1 and 1 μm .

A study by Seipenbusch et al. (2008) mimicked the fate of ENMs during fugitive diffuse emissions from a reactor during production of platinum nanoparticles and found that the lifetime of primary nanoparticles in the atmosphere is limited by coagulation, so that larger aggregates and agglomerates are formed rapidly once nanoparticles enter the air, particularly in the presence of coarser background aerosols. Collisions between NPs within their own size class (coagulation), and if present, with background aerosols were identified as

the most important mechanism driving the change in particle size and number concentration (Seipenbusch et al. 2008). Most importantly, at high aerosol background concentrations, virtually all of the platinum particles were attached to the background aerosols, whereas at low background concentrations many of the NPs remained in primary particle form (Seipenbusch et al. 2008), indicating that in the atmosphere, nanoparticles may enter soil and water in both their primary particle and agglomerated forms. At low NP concentrations, coagulation may be insignificant, so that most NPs will either be individual particles or, more likely, attached to larger aerosols (Maynard and Zimmer 2003).

ENMs in the atmosphere will be removed via wet or dry deposition. Dry deposition removes particles through transfer to air-surface interfaces. This process is mainly driven by Brownian diffusion and inertial impaction (Friedlander and Pui 2004). Under dry deposition, the size of the ENMs and their aggregates contribute to the rate of removal. This is because gravitational sedimentation velocities are proportional to the particle's diameter and density (Friedlander and Pui 2004). Thus sedimentation rates should correlate with aggregation rates, much as in aquatic systems, and will be lower for smaller particles than for larger particles. A number of workplace air studies found that dry deposition tends to occur within just a few hours. For example, Bello et al. (2009) found that dry cutting as a method of manufacturing CNTs does release nanoscale particles into the air, however, within just a few hours, concentrations decrease to within baseline levels; Tsai et al. (2009) found that air concentrations of ENMs released from under a fume hood return to baseline within 0.5–2 h for both nano- Al_2O_3 and Ag; and Gong et al. (2009) measured the surface deposition loss rates of diesel exhaust particles and found a loss rate of $\sim 10/\text{h}$ for 30 nm particles and $\sim 4/\text{h}$ for 100 nm particles.

Wet deposition is the removal of particles through precipitation (Laakso et al. 2003). This can occur by nucleation scavenging (i.e., rain out, the inertial capture of dust particles by falling rain drops) and aerosol-hydrometeor coagulation (i.e., washout through formation of raindrops around particles as condensation nuclei) (Jacobson 2003). Particle size also determines the efficiency of washout of airborne particles by rain. Typically, the rainfall washout coefficient is larger for smaller particles (Pranesh

and Kamra 1997), for the coefficient would be larger for nanometer sized particles than micrometer sized particles.

Environmental conditions may also affect atmospheric particle size and fate. However the results are not completely consistent. For example, one study found that higher particle number concentrations persisted at high temperatures (Chang et al. 2004). Others found that higher particle concentrations were observed in winter because of the combination of lower temperatures and less dilution (Jeong et al. 2004; Stanier et al. 2004). Similarly Tsai et al. (2009) found that low humidity caused more small agglomerates to become airborne during handling of nano- Al_2O_3 .

Fate and transport in water

Current predictions indicate that globally as much as 66,000 metric tons of ENMs are released directly to surface waters every year (Keller and Lazareva 2013). The fate and transport of ENMs in water largely depends on the chemical properties of the water. In this review, we consider the effects of freshwater, stormwater, groundwater, and seawater on rates of aggregation, sedimentation, and dissolution. Some studies considered in this review did not specifically use any of the above four water types; where necessary we categorized the water using the IS or concentration of NOM according to the ranges in Keller et al. (2010) and Quik et al. (2013). Differences in aquatic characteristic can significantly impact the rate of many fate and transport processes. For example, the IS and concentration of NOM present in seawater versus freshwater will impact rates of aggregation, sedimentation, and dissolution for some ENMs. Variations in surface charge, surface coating, and shape can also alter the fate of ENMs in the environment. Transformations processes such as oxidation, sulfidation, and interactions with phosphate, all frequently present in aquatic systems, will also have a significant effect on aggregation, dissolution, and as a result toxicity.

Aggregation in water

Particle aggregation refers to the formation of ENM clusters in colloidal suspension. This is most likely to occur during the use phase of the ENMs while the ENM concentration is high. During this process,

particles dispersed in a liquid adhere to one another via homoaggregation or to other particles via heteroaggregation (Praetorius et al. 2013; Zhou et al. 2012a). Following release to water most NPs will aggregate to some degree and the behavior of the resulting aggregates is expected to be very different from that of primary NPs (Zhang et al. 2008). The degree of aggregation and the size range of the aggregates depend on the characteristics of the particle, the concentration of the particles, and the characteristics of the environmental system (Dunphy Guzman et al. 2006; Phenrat et al. 2007). NP aggregation and deposition behavior will dictate particle transport potential and thus the environmental fate, bioavailability, and potential ecotoxicological impacts of these materials (Blaser et al. 2008; Petosa et al. 2010; Liu and Cohen 2014).

Aggregation of spherical NPs can generally be described using extended Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Elimelech et al. 1998; Isrealachvili 1992; Stebounova et al. 2011; Wang and Keller 2009). The basic DLVO theory predicts that the stability of NPs suspended in aqueous environments can be evaluated as the balance between attractive van der Waals (VDW) forces and repulsive electrical double layer (EDL) forces (Elimelech et al. 1998; Isrealachvili 1992). A stable suspension requires a dominant repulsive force to maintain dispersion of particles. However, if attractive forces dominate, or particles collide with sufficient energy to overcome repulsion, they will form aggregates that then sediment out of suspension (Elzey and Grassian 2010). Extended DLVO theory takes into account non-electrostatic ion-specific forces such as acid–base, steric, magnetic, and hydrodynamic forces (Hyung and Kim 2008; Petosa et al. 2010; Stebounova et al. 2011; Zhu and Cai 2012), all of which can play important roles in the aggregation of ENMs. Additional considerations need to be made for non-spherical NP morphologies (Zhou and Keller 2010, Zhou et al. 2013).

In theory, aggregation rates can be calculated using the ENM collision rate and attachment efficiency (Praetorius et al. 2012; Quik et al. 2014). The attachment efficiency represents the fraction of collisions between particles that result in attachment (Pelley and Tufenkji 2008), since simply making contact with another particle does not ensure that aggregation will occur as various factors (such as the

EDL) may prevent aggregation (Pelley and Tufenkji 2008). Attachment efficiency depends on environmental conditions such as pH, IS, ion valence, temperature, and ENM and other particle concentrations (Arvidsson et al. 2011). Additionally, recent research indicates that heteroaggregation, rather than homoaggregation, is far more likely in the environment (Quik et al. 2014). However, when nanoparticles first enter a water body, the release point may contain concentrations high enough to result in homoaggregation. While the same physical processes and environmental conditions apply to both homoaggregation and heteroaggregation, the ENM to natural particle attachment efficiencies and the much higher frequency of collisions may dominate the removal of ENMs (Zhou et al. 2013).

The stability of NPs in aquatic environments depends on the properties of the ENM itself (size, charge, zeta potential, coatings, ENM point-of-zero charge (PzC), particle density, and magnetization), the ambient environmental characteristics (pH, IS, NOM, suspended particle concentration), and the initial ENM concentration. Surface charge and aggregation tend to vary with pH, where the further the environmental pH is from the ENM's PzC, the farther the surface charge is from zero. This increases their stability, since like charges will repel (Adeleye et al. 2013; Judy et al. 2011; Reed et al. 2012; Wang et al. 2011). However, high IS can minimize the forces keeping NPs separate and cause aggregation and sedimentation (French et al. 2009; Handy et al. 2008) even for a pH that is far from the PzC. Divalent ions, such as calcium and magnesium, are prevalent in many aquatic systems, and affect aggregation of ENMs by more effectively compressing the EDL surrounding the NPs (French et al. 2009; Handy et al. 2008). This allows attractive forces to dominate, so that the primary particles floc and form aggregates that eventually sediment out of solution (Elzey and Grassian 2010). Thus, the zeta potential is a key parameter for predicting whether an ENM will be stable or will tend to aggregate in a given aqueous matrix. This is valid for homo- and heteroaggregation (Zhou et al. 2013).

Zeta potentials for Ag, CeO₂, and NiO, and nZVI, and TiO₂ are generally fairly negative (>−20 mV) in natural waters, particularly in freshwater (Delay et al. 2011; Griffitt et al. 2008; Quik et al. 2010; Sunkara et al. 2010). The zeta potential for nZVI also remains relatively negative even at high IS and pH ranging

from 7 to 10 (Adeleye et al. 2013; Yin et al. 2012). Similarly, the zeta potential for Al_2O_3 is generally fairly negative even in the presence of some IS at pH ranging from 4 to 9 (Ghosh et al. 2010; Griffith et al. 2008). Conversely, the zeta potential for TiO_2 at 10 mM CaCl_2 is close to zero at pH 7 (Petosa et al. 2012). The zeta potential for ZnO seems to vary significantly from very positive to very negative at pH values ranging from 4 to 10 (Jiang et al. 2009a, b; Petosa et al. 2012; Reed et al. 2012). The zeta potentials for Au and Cu/CuO tend to be close to zero for a pH between 5.5 and 8.5, except in groundwater for Au and in algal growth media for Cu/CuO (Griffith et al. 2008; Hitchman et al. 2013; Judy et al. 2011; Wang et al. 2011). At $\text{pH} < 7$, increasing the IS increases aggregation for Ag, whereas at $\text{pH} > 7$, increasing the IS has minimal effect on the rate and extent of aggregation as well as the zeta potential (Badawy et al. 2010). Furthermore, change in pH had minimal effect on the zeta potential of electrostatically stabilized Ag NPs and only a moderate effect on the zeta potential of uncoated particles (Badawy et al. 2010). However, changes in pH have a strong effect on electrosterically stabilized Ag NPs zeta potential, though changes in IS do not significantly affect stability (Badawy et al. 2010). These results indicate that both pH and IS will strongly determine surface charge and thus the extent of aggregation in water. Similar results were found for TiO_2 , where pH and thus surface charge and aggregate size dominate nanoparticle interactions with themselves and the environment (Dunphy Guzman et al. 2006).

Aggregation is generally regarded as irreversible (Arvidsson et al. 2011). Zhang et al. (2008) found that it is very difficult to disaggregate metal oxide NPs and neither sonication nor dispersants were effective in fully disaggregating these ENMs. However, Zhou et al. (2012a, b) found that fractal agglomeration of TiO_2 and other metal oxide ENMs was partially reversible during exposure to sunlight and diurnal temperature variations. Silver agglomerates were also found to break apart with agitation and the primary particles were easily resuspended (Elzey and Grassian 2010). Thus partial disaggregation can occur under natural conditions.

Stabilization of ENMs by surface coatings may cause them to remain in the water column and increase their transport distances (Christian et al. 2008). Stabilizers may be used in the manufacturing process

to reduce aggregation and enhance the dispersion of engineered NPs, which decreases the attachment efficiency. Stabilizers work either by electrostatic repulsion, where a charged stabilizer increases repulsion between particles or steric hindrance, where the stabilizer physically impedes particle adhesion (Baalousha 2009; Illés and Tombácz 2006). A wide range of stabilizers have been found to be effective including thiols, carboxylic acids, surfactants, and polymers. For example, Kvitek et al. (2008) found that PVP was the most effective polymer stabilizer for Ag and that the addition of a charged group to the polymer can increase electrosteric stabilization. Adsorbing charged ions such as pyrophosphate onto the surface of TiO_2 NPs stabilizes the NPs and decreases aggregation (Jiang et al. 2009a, b). Polyelectrolyte surface coatings can be used to inhibit nZVI aggregation and enhance mobility (Kim et al. 2009; Sirk et al. 2009). The stabilizers not only affect the behavior of the NP within a product but can also enhance the mobility of ENMs in the environment (Tungittiplakorn et al. 2004).

The effect of NOM on aggregation is complex since it can both enhance and reduce aggregation, and is usually interconnected with other ambient environmental properties (Arvidsson et al. 2011). The presence of NOM generally results in a more negatively charged particle, enhancing particle stability via electrosteric stabilization mechanisms as well as steric hindrance (Chen et al. 2007; Fabrega et al. 2009; Gilbert et al. 2007). ENM interaction with NOM is best described as a heteroaggregation process, where ENMs collide with NOM on the basis of their respective diffusion velocities and adhere to NOM depending on the surface properties of both (Praetorius et al. 2012). NOM can also affect the structure of aggregates. For example, iron oxide in the absence of NOM forms porous aggregates, whereas in the presence of NOM, it forms compact aggregates (Baalousha et al. 2008). High concentrations of NOM have been shown to induce partial disaggregation of Ag at 10 mg NOM L^{-1} and full disaggregation at higher concentrations. However, these concentrations of NOM are not frequently observed in the environment and thus full disaggregation by NOM alone is unlikely.

Studies conducted on the aggregation of ENMs in various types of waters with a range of IS and NOM concentrations can be categorized by their aggregation

Fig. 2 Aggregation time frames of ENMs in different water types (*asterisk = coated*). The current commonly predicted rate of aggregation for ENMs in stormwater, freshwater, groundwater, and seawater are delineated. Within each rate division, there is no distinction between which ENMs may aggregate faster or slower. The asterisks indicate if most studies used to estimate the rate of aggregation of a specific ENM and water type used a coated ENM

Residence Time	Stormwater	Freshwater	Groundwater	Seawater
Months	Ag*	Ag*		
	Au*	Au*		
	CeO ₂	CeO ₂		
	C ₆₀	C ₆₀	C ₆₀	SiO ₂
	FeO/Fe ₂ O ₃	FeO/Fe ₂ O ₃	MWCNTs	
	MWCNTs	MWCNTs	SiO ₂	
	SiO ₂	SiO ₂		
	TiO ₂	TiO ₂		
Weeks	ZnO	ZnO		
	nZVI*	NiO	Au*	
	SWCNTs	nZVI*	FeOOH	CuO
Days		SWCNTs	Latex	FeO/Fe ₂ O ₃ *
			SWCNTs	
			Ag*	Ag*
		Al ₂ O ₃	CeO ₂	C ₆₀
			CuO	FeOOH
Hours			NiO	SWCNTs
			TiO ₂	
			FeO/Fe ₂ O ₃	Au*
			nZVI*	CeO ₂
			ZnO	MWCNTs
			nZVI*	
			TiO ₂	
			ZnO	

time frame (hours, days, weeks, months or greater) and water type (Fig. 2). The ENMs are listed alphabetically within each rate category. Au and Ag NPs in these studies are coated with organics, typically PVP or citrate. Deviations and exceptions to these categorizations are identified in Supplemental Table S2. Faster aggregation indicates that NPs will not remain in the water column for long (hours to days) and thus exposure to most pelagic aquatic species will be limited. In addition, aggregation will lower the transformation and reactivity of NPs since less effective surface area is exposed.

Most NPs are largely stable in freshwater and stormwater with some aggregation observed for Al₂O₃ (Pakrashi et al. 2012), NiO (Gong et al. 2011), nZVI (Keller et al. 2012; Saleh et al. 2008a, b), and SWCNTs (Bennett et al. 2013; Wang et al. 2008a, b). Sorption and change in electrophoretic mobility have been shown to occur on exposure of NOM to metal and metal oxide NPs (Fabrega et al. 2009). Keller et al. (2010) found that NOM adsorbed onto TiO₂, ZnO, and CeO₂ and significantly reduced their aggregation, stabilizing them under many conditions.

Even within a water type, variations in NOM concentration will result in varied aggregation rates (Hammes et al. 2013; Liu et al. 2013a, b). This is consistent with our findings that many metal oxides are less likely to aggregate in stormwater and freshwater given their high NOM content. However, with the exception of SiO₂ (Zhang et al. 2009), most NPs will aggregate fairly rapidly in seawater. This is due to the high IS, which compresses the EDL, and low concentration of NOM, which does not provide sufficient electrostatic stabilization in seawater. Groundwater had the most variable results, with some ENMs aggregating rapidly, such as FeO/Fe₂O₃ (Zhang et al. 2008), coated nZVI (Keller et al. 2012; Yin et al. 2012), and ZnO (Zhang et al. 2008; Zhou and Keller 2010), while others remained fairly stable over the long term, such as Au (Stankus et al. 2010; Unrine et al. 2010), C₆₀ (Chen and Elimelech 2007; Fortner et al. 2005), FeOOH (Gilbert et al. 2007), SiO₂ (Zhang et al. 2008, 2009), and SWCNTs (Bennett et al. 2013). This likely is due as much to an individual ENM's characteristics as it is to the high variability in the IS of groundwater and difficulty categorizing water samples as groundwater

equivalent. Many groundwater studies are conducted in the laboratory with artificial groundwater under unfavorable aggregation conditions that may not be representative of natural systems. For ZnO and nZVI, the fast aggregation in groundwater is similar to the fast aggregation in seawater, and thus may be explained by the IS of groundwater. However, aggregation of FeO/Fe₂O₃ was much slower in seawater (Chen et al. 2006) than in groundwater (Zhang et al. 2008), so there may be other factors at work.

Sedimentation in water

ENMs can be deposited to the sediment compartment via gravitational settling of aggregates or settling of ENMs sorbed to NOM or other suspended particles. There is a strong correlation between aggregation and sedimentation since particle size is such a strong determining factor in the rate of sedimentation. However, particle buoyancy is also a factor. Generally there is a delay between aggregation and sedimentation, which results in rates of sedimentation that are slightly slower than those for aggregation. In many instances, initial aggregation is so fast that it results in almost simultaneous sedimentation. Aggregate particle size is a major factor affecting the rate of sedimentation along with ambient environmental characteristics, such as the presence of NOM or other stabilizing agents and the IS or presence of different electrolytes as well as the viscosity of the fluid and the initial ENM concentration (Phenrat et al. 2008; Quik et al. 2011). The rate of sedimentation depends on the density and size of the particles, regardless of whether they are primary particles or complex aggregates, as well as the density of the fluid (Praetorius et al. 2012). Discrete settling can be estimated using Stoke's law (Quik et al. 2011). For sedimentation to occur, the settling velocity must be equal to or greater than the critical settling velocity for the system (Praetorius et al. 2012; Westerhoff et al. 2013). This is valid for aggregates as well as primary particles. Phenrat et al. (2007) found that the rate of sedimentation tends to follow three phases: an initial slow phase as aggregation is still occurring; a fast phase; and then another slow phase where the overall concentrations of particles is low as a result of sedimentation.

In addition to ENM aggregation, collisions of ENMs with suspended particles, such as clays, will lead to accelerated aggregation and sedimentation

(Zhou et al. 2012a). This is dependent on the nature of the suspended particle and whether attachment of the ENM to the suspended particle is highly favorable, unfavorable, or somewhere in between. For example, at low pH values and intermediate IS, clay particles with positive surface charges reduce the stability of negatively charged Ag and positively charged TiO₂ ENMs (Zhou et al. 2012a).

As with aggregation, a review of the literature was conducted on the sedimentation rates of ENMs in various types of waters based on their IS and NOM concentration. These were categorized by residence time and water type (Fig. 3) with details on specific sources provided in Supplemental Table S3. Faster sedimentation (i.e., within hours to days) results in a shorter residence time in the water column and will result in lower exposure doses to species living in the water column, with corresponding accumulation in sediment (Klaine et al. 2008). Slower sedimentation (i.e., multiple weeks or longer) indicates greater transport distances, but with increasing dilution over time as the ENMs move away from the source via advection and dispersion.

In general, sedimentation is faster in seawater than in the other water types, much as with aggregation. Also, there are fewer notable differences in rates of sedimentation for stormwater, freshwater, and groundwater than there are for aggregation. This is because of ENMs such as NiO (Griffitt et al. 2008; Zhang et al. 2008), nZVI (Saleh et al. 2008a, b; Schrick et al. 2004), and ZnO (Franklin et al. 2007; Keller et al. 2010; Zhang et al. 2008; Zhou and Keller 2010; Zhou et al. 2012b) have similar sedimentation rates for groundwater, stormwater, and freshwater. Further, Ag (Chinnapongse et al. 2011; Griffitt et al. 2008; Lowry et al. 2012a, b), nZVI (Schrick et al. 2004), and ZnO (Franklin et al. 2007; Keller et al. 2010; Zhou and Keller 2010; Zhou et al. 2012b) appear to have sedimentation rates that are marginally faster than the rate of aggregation in both freshwater and stormwater (weeks instead of months, or days instead of weeks). CeO₂ (Keller et al. 2010; Quik et al. 2010; Zhou et al. 2012b) and FeO/Fe₂O₃ (Zhu et al. 2012) have sedimentation rates that are faster than the aggregation time frame in freshwater (days or weeks instead of months). This may be a result of different ENM primary particle sizes or coatings in the various studies.

Fig. 3 Sedimentation time frames of ENMs in different water types, as measured by the residence time in the water column (asterisk = coated). The current commonly predicted rate of sedimentation for ENMs in stormwater, freshwater, groundwater, and seawater are delineated. Within each rate division, there is no distinction between which ENMs may sediment faster or slower. The asterisks indicate if most studies used to estimate the rate of sedimentation of a specific ENM and water type used a coated ENM

Residence Time	Stormwater	Freshwater	Groundwater	Marine
Months	Au*	Au *		
	CeO ₂	C ₆₀	C ₆₀	
	C ₆₀	MWCNTs	FeOOH	SiO ₂
	MWCNTs	SiO ₂	SiO ₂	
	SiO ₂	SWCNTs		
Weeks	SWCNTs	TiO ₂		
	TiO ₂	Ag*	Au*	
		CeO ₂	CeO ₂	Au
	Ag*	CuO	NiO	
	ZnO	NiO	ZnO	
Days		ZnO		Ag*
	nZVI*	FeO/Fe ₂ O ₃	nZVI*	C ₆₀
		nZVI*	TiO ₂	FeOOH
				nZVI*
				ZnO
Hours				CeO ₂
			FeO/Fe ₂ O ₃	MWCNTs
				TiO ₂

As with aggregation, these results indicate that sedimentation will occur more quickly in seawater than other natural waters, whereas in freshwater and stormwater, particles are likely to remain suspended for extended lengths of time. This will lead to higher exposures of freshwater aquatic species to ENMs and higher exposures of benthic marine species to ENMs.

Dissolution in water

Dissolution is important for some ENMs, though it is very specific to the ENM and sometimes the aqueous medium. It involves the release of dissolved ions from the NP, even within an aggregate (Quik et al. 2011). Dissolution is a surface-controlled process that is dependent on the surface area of the ENM and the concentration of the dissolved ions near the particle's surface (Quik et al. 2011). Greater surface to volume ratios of NPs generally result in increased dissolution (Quik et al. 2011). Additionally, most metal NPs show increased dissolution at extreme pH values, particularly low pH (Quik et al. 2011). This is because solution pH affects the dissociation equilibrium of a complexing agent, the protonation or hydroxylation of the ionic groups released by NP dissolution, and NP interfacial free energy (Zhang et al. 2010).

The resulting extent of dissolution is determined by the thermodynamics of the system; if the overall free energy is negative, dissolution will occur and if the solubility product coefficient is positive (K_{sp}). Essentially, energy is needed to break the bonds between ions in NPs. The free energy is determined by the chemical bonds present in the system. Thus, dissolution rate is primarily a function of the bond strength between atoms on the NP surface; it can be accelerated by surface reactions that strip atoms from the surface (Stumm and Morgan 1981). Dissolution rate is also controlled by the metal ion concentration gradient between the particle surface and the bulk medium, as well as the concentration of other dissolved ions that can react with metal ions released from the NP (Misra et al. 2012). If the released ions (e.g., Ag⁺) can react quickly with other water constituents (e.g., Cl⁻) near the NP surface, this will maintain a high gradient resulting in faster overall dissolution, as observed with Ag NPs in seawater (Thio et al. 2012). Thus, dissolution is also controlled by the characteristics of the surrounding media (pH, IS, water hardness), presence of organic components (NOM, polysaccharides, proteins) that can bind released ions, and sulfides and phosphates which form strong bonds with released metal ions.

NP size has also been found to affect the rate and extent of dissolution, since surface area increases with decreasing size, exposing more atoms per volume to the surrounding medium. For both CuO and coated Ag NPs, decreasing the size of the NPs increases the dissolution (both the rate and the equilibrium concentration), whereas the size of ZnO nanoparticles does not appear to significantly increase dissolution (Baek and An 2011; Franklin et al. 2007; Levard et al. 2012; Liu et al. 2011; Ma et al. 2012; Misra et al. 2012; Mortimer et al. 2010; Navarro et al. 2008; Xia et al. 2008).

Surface chemistry can also impact rates of dissolution. Functional groups on the NP surface often determine solubility (Verma and Stellacci 2010). For example, Au NPs capped with the appropriate surface monolayer do not readily dissolve (Zhu et al. 2010). A silica coating on hydrophobic Ag, Au, and Fe₃O₄ increased the stability to weeks or even months (Jana et al. 2007).

NOM can act as a complexing agent that decreases the dissolution of some ENMs. For example, ENMs can bind to NOM, colloids, or other sediments while dissolution is still occurring (Allen and Hansen 1996). One study found that the small size of fulvic acid results in little impact on Ag particle dissolution; however, larger molecular weight humic acids appear to decrease stability and increase dissolution (Li et al. 2010a, b, c). As with NOM, ENM surface oxidation or sulfidation can decrease dissolution rates for ENMs such as Ag, which can also decrease toxicity (Levard et al. 2011). This is because oxidation and sulfidation can produce coatings on the ENMs which hinder the release of the metal ions from the inner core of the ENM.

Many studies have been conducted on the dissolution rates of ENMs in various types of waters based on their IS and NOM concentration. These were categorized by dissolution time frame (hours, days, weeks, months, or greater) and water type (Fig. 4). Carbonaceous NPs such as C₆₀, MWCNTs, and SWCNTs do not dissolve to any significant extent and thus are not included in this study. However, in many cases carbonaceous NPs include metal catalyst residuals, which can leach ions to a significant extent (Adeleye and Keller 2014; Bennett et al. 2013). The carbonaceous NPs are not included in Fig. 4, since the type of metal ions and their dissolution extent and time frame depends on the method of synthesis. The ENMs are

listed alphabetically within each rate category. The categories are based on many different studies and there are deviations and exceptions to some of these categorizations, identified in Supplemental Table S4. Faster dissolution means decreased NP concentrations and increased dissolved ions.

With the exception of ZnO in seawater (Fairbairn et al. 2011; Li et al. 2013; Miller et al. 2010; Xia et al. 2008) and freshwater (Franklin et al. 2007; Li et al. 2013; Mortimer et al. 2010; Reed et al. 2012), NP dissolution is generally slow, occurring over the course of weeks or months, if at all. Dissolution of ZnO is highly pH dependent and the presence of phosphate can significantly alter the rate of dissolution so that it can be either very high or very low (Blinova et al. 2010; Montes et al. 2012). ENMs such as Au (Griffitt et al. 2008; Hitchman et al. 2013), CeO₂ (Cornelis et al. 2011; Gaiser et al. 2011; Montes et al. 2012), and TiO₂ (Griffitt et al. 2008; Keller et al. 2010; Miller et al. 2010) are not expected to dissolve to any significant extent, even over long periods of time regardless of water type. There is a slight increase in rate of dissolution from weeks to months as IS increases and NOM decreases, but this could also be driven by the presence of Cl⁻ and other ions that enhance precipitation of the dissolved ions, as in saline media. These studies also indicate that most NPs are unlikely to dissolve in stormwater, particularly due to the short residence times of ENMs in this medium.

It is also worth noting that the toxic effect observed with some of these ENMs, such as CuO and ZnO, strongly correlate with the fraction of ENMs dissolved in the aquatic media (Aruoja et al. 2009; Blinova et al. 2010; Li et al. 2013). While faster dissolution may mean that the NPs do not remain in particle form, the ionic form of a metal is often toxic and this may have as much or more significant effects if dissolved than in particle form. At the same time, dissolution of ENMs can decrease the hydrodynamic diameter of the NPs, which may increase their toxicity (Li et al. 2010a, b, c).

These results indicate that dissolution may occur marginally faster in seawater and groundwater than in stormwater or freshwater, with some exceptions (e.g., Ag). This means that many ENMs will remain in NP form, within aggregates, for significant periods of time. If they remain suspended, as they do in some water for Au, CeO₂, Cr₂O₃, CuO, NiO, SiO₂, and TiO₂ (Fig. 3), this will lead to high exposure of aquatic

Residence Time	Stormwater	Freshwater	Groundwater	Marine
Months	Au*	Au*	Au*	Au*
	FeO/Fe ₂ O ₃	CeO ₂	CeO ₂ *	CeO ₂
	NiO	FeO/Fe ₂ O ₃	CuO	CuO
	TiO ₂	TiO ₂	NiO	TiO ₂
Weeks		Ag*		
	CuO	Al ₂ O ₃	Ag*	Ag*
	ZnO	CuO	ZnO	Al ₂ O ₃
		NiO	nZVI*	NiO
		PbS		
Days		ZnO		
Hours				ZnO

Fig. 4 Dissolution time frames of ENMs in different water types (*asterisk* = coated). The current commonly predicted rate of dissolution for ENMs in stormwater, freshwater, groundwater, and seawater are delineated. Within each rate division, there

is no distinction between which ENMs may sediment faster or slower. The asterisks indicate if most studies used to estimate the rate of dissolution of a specific ENM and water type used a coated ENM

species to particulate ENMs rather than dissolved ENMs. However, if they tend to sediment quickly in some waters, as with Ag, FeO, and nZVI (Fig. 3), this will lead to high exposure of benthic marine species to particulate ENMs rather than dissolved ENMs. The exception is ZnO, which is the only ENM predicted to dissolve rapidly in seawater and freshwater. Given the slower sedimentation rates relative to the dissolution rates of ZnO, one can expect that water column species will have a higher probability of exposure to dissolved Zn²⁺ ions. However, Zn²⁺ can form precipitates with phosphate (Kandah 2004), which can reduce the dissolved Zn²⁺ concentrations.

Transformations

Environmental transformations of NPs will also affect their physical and chemical properties and thus their fate and toxicity. Significant transformation processes may include oxidation, sulfidation, and reactions with phosphorous. In general, many transformations tend to result in less reactive nanoparticles that are less likely to dissolve and may thus be less toxic.

Many metallic NPs can and likely will be oxidized in oxic waters. For example, nZVI is highly redox active and generates reactive oxygen species (ROS) through Fenton chemistry (Joo and Zhao 2008). Through oxidation, nZVI is transformed to magnetite (Fe₃O₄) or other iron oxides, releasing Fe²⁺ and Fe³⁺ which can further react (Adeleye et al. 2013). There is

extensive evidence that nZVI in the presence of oxygen can induce oxidative transformations of a variety of organic and inorganic species including heavy metals, pesticides, and chlorinated organic compounds (Feitz et al. 2005; Joo and Zhao 2008; Joo et al. 2004). Ag is also oxidized, releasing Ag⁺, which can then react with Cl⁻ to form AgCl even in freshwater, since it is more thermodynamically favorable than Ag₂O (Levard et al. 2012). Under oxic conditions, little or no sulfide is present, but as the AgCl precipitates out and is deposited on sediments, Cl⁻ can exchange with S²⁻ to form Ag₂S (Levard et al. 2012). Nano-Cu particles can also readily oxidize, forming various complexes depending on water chemistry. For example, in freshwater, after dissolving nano-Cu may form carbonate complexes such as CuCO₃ and Cu(CO₃)₂²⁻ or hydroxide complexes such as Cu(OH)₂, Cu(OH)⁺, and Cu₂(OH)₂²⁺ (Flemming and Trevors 1989). The predominant species formed depend significantly on the concentrations of OH⁻ and CO₃²⁻ (i.e., pH and water hardness) (Adeleye et al. in preparation).

Sulfidation is an important transformation process affecting metal and metal oxide NPs by replacing ions with sulfide, under low redox conditions such as sediments and certain phases of wastewater treatment. The concentration of sulfides controls the rate and extent of sulfidation. Typical sulfide concentrations in oxic waters may lead to very low rates of sulfidation. High sulfide levels are usually associated with

anaerobic conditions, but if oxygen is completely absent, the results of Liu et al. (2011) indicate that sulfidation will actually be suppressed. In anaerobic waters, ZnO NPs can be transformed to ZnS through the dissolution and reprecipitation of zinc ions (Ma et al. 2013), Cd NPs can be transformed to CdS (Cabot et al. 2008), and PVP-coated Ag NPs may be transformed to silver sulfide (Ag_2S) sometimes via oxysulfidation (Levard et al. 2011; Liu et al. 2011; Reinsch et al. 2012). Near complete conversion of Ag to Ag_2S was found in wastewater treatment plant effluent, indicating that Ag_2S will be formed in sulfur rich, reducing environments (Kim et al. 2010). This transformation can affect surface properties of NPs in terms of surface charge and dissolution rate. Both may affect the reactivity, transport, and toxicity (Levard et al. 2011). Sulfidation of Ag has been shown to significantly reduce toxicity due to the lower solubility of silver sulfide (Levard et al. 2012). Sulfidation is very likely to occur for other metal and metal oxide NPs, such as CuO, Fe, and Pb, given the low K_{sp} for metal sulfides (Stumm and Morgan 1981).

The extent of sulfidation is strongly dependent on sulfide concentration. For ZnO, close to 100 % was converted to ZnS within 5 days in the presence of sufficient sulfide concentrations (Ma et al. 2013). Similarly, for Ag, in systems with a ratio of S/Ag as low as 0.2, more than 15 % of the Ag is found as Ag_2S within 24 h (Levard et al. 2011). The presence of sulfides may also cause rapid aggregation and sedimentation (Ma et al. 2013). This concurs with the fact that the point-of-zero charge increases with increasing sulfur for Ag, though this will not necessarily lead to an increase in aggregation (Levard et al. 2011). As soon as a very small amount of sulfur is added to the system, (S/Ag of 0.019) particles begin to aggregate and form chain-like structures, so that along with transforming to Ag_2S , the presence of sulfur appears to cause rapid aggregation and sedimentation (Levard et al. 2011; Reinsch et al. 2012). This will limit mobility in aquatic systems with sulfide. Sulfidation also decreases the rate and extent of dissolution. For ZnS, there was only a significant decrease in dissolution at Zn/S ratios above 0.616 (Ma et al. 2013) whereas even the lowest tested presence of Na_2S decreases dissolution of Ag NPs by a factor of 7 (Levard et al. 2011). In a high sulfide environment, the concentration of Ag^+ was found to decrease from less than 1 mg/L to less than 10 ppb (Reinsch et al. 2012).

Environmental characteristics such as pH, IS, and the presence of NOM can alter the rate and effect of sulfidation. Much as NOM alters the stability of ENMs by decreasing aggregation, sedimentation, and dissolution; it was also found to slightly increase sulfidation of Ag (Liu et al. 2011). A low IS may minimize aggregation of Ag_2S and reducing the pH increases the rate of Ag sulfidation (Liu et al. 2011; Reinsch et al. 2012). Sulfidation may also be more likely to occur under anaerobic conditions, and while metal sulfides have been found in aerobic waters their persistence may be short (Luther and Tsamakis 1989; Rozan et al. 2000). The presence of a surface coating on Ag does not appear to have any effect on the rate of sulfidation (Li et al. 2010a, b, c).

The effects of phosphate have largely been ignored despite the wide presence of phosphate in aqueous environments likely interacting with ENMs entering those same systems. Only a few studies have looked specifically at how the presence of phosphate affects the fate, transport, and toxicity of ENMs (Daou et al. 2007; Lv et al. 2012). Phosphate at a low concentration rapidly and substantially reduced the release of Zn^{2+} into aqueous solution. One study found that low concentrations of phosphate rapidly reduced the dissolution of ZnO by transforming the ZnO to zinc phosphate (Lv et al. 2012). Another study found that phosphate in phosphate buffered saline media either reacted with the ZnO or strongly attached to the surface of the ZnO particles (Li et al. 2011a, b, c). This may result in decreased toxicity from ZnO (Lv et al. 2012; Li et al. 2011a, b, c). Phosphate adsorption to magnetite nanoparticles was also found to occur and to inhibit dissolution, though the study only considered a low pH environment (Daou et al. 2007). A study on the transformation of ZnO and Ag in wastewater treatments plants found that Ag was converted to Ag_2S , indicating that Ag is less likely to react with phosphates; whereas ZnO was transformed to ZnS, $\text{Zn}_3(\text{PO}_4)_2$, and Zn associated with Fe oxyhydroxides (Ma et al. 2014). Interestingly, a study on the effect of phosphate impurities in TiO_2 found that its presence improved the suspension stability of TiO_2 (Liu et al. 2013a, b). This suggests a small possibility that TiO_2 will be more stable in water with phosphate.

Fate and transport in soil

Soils are characterized by the presence of a heterogeneous mixture of gas, liquid, and soil phases, the

interfaces between them, and the presence of organic matter and microbial communities. The complex nature of soil systems mean that our understanding of processes affecting the fate of ENMs in soil is limited, especially in unsaturated soils. This is due in part to the complexity of measuring how ENMs interact with unsaturated soil as opposed to groundwater (Tiede et al. 2009; Tourinho et al. 2012). As in water, most ENMs in soil are likely to aggregate, sorb to surfaces, sediment, and dissolve (Dunphy Guzman et al. 2006; Franklin et al. 2007; Tourinho et al. 2012), which can be determined by the estimated rates of aggregation, sedimentation, and dissolution in groundwater (Figs. 2, 3, 4), with some possible exceptions. In unsaturated soil, work with colloids suggests that ENMs will likely be trapped in the air/water interface (Sirivithayapakorn and Keller 2003a).

Transport in porous media can be described by three mechanisms: (i) direct interaction of ENMs with soil; (ii) sedimentation due to gravity; and (iii) diffusion due to Brownian motion (Dunphy Guzman et al. 2006; Fang et al. 2009). Gravitational sedimentation will be negligible without significant aggregation (Fang et al. 2009). For transport to occur, forces that cause ENMs to attach to soil particles, such as electrostatic forces, VDW forces, hydrodynamic forces, hydration/structural forces, hydrophobic forces, and steric interactions must be minimized (Bradford et al. 2002; Schrick et al. 2004). A number of studies have determined that the fate of ENMs in soil is strongly dependent on primary particle size (Darlington et al. 2009; Tufenkji and Elimelech 2004), aggregate particle size (Darlington et al. 2009), and surface charge, as well as environmental conditions such as pH, IS, the presence of NOM, clay content, and flow velocity (Tourinho et al. 2012). These characteristics will affect physical and chemical processes that affect ENMs such as aggregation and dissolution (Tourinho et al. 2012).

Transport is strongly dependent on the size of the ENMs; it is the aggregate size, not the primary particle size, which tends to correlate with mobility (Darlington et al. 2009). One study with Al_2O_3 found that at larger primary particle size and larger aggregate size, ENMs are less mobile (Darlington et al. 2009). Another study confirmed that attachment efficiency increased with increasing particle size for latex NPs (Tufenkji and Elimelech 2004). Conversely, a study with SiO_2 found that smaller NPs resulted in higher

relative retention in column experiments, which could be caused by the relative charge on the NPs (Wang et al. 2012a, b). There are likely two mechanisms responsible for this observed size effect: (i) size directly affects the interaction energy between ENMs and soil surfaces, and (ii) size may influence the physical and chemical properties of ENMs, since smaller particles are generally more reactive (Wang et al. 2012a, b). Surface charge can affect particle–particle interactions as well as particle–soil interactions (Saleh et al. 2008a, b). As with water, when an ENM is in a system where the pH causes the zeta potential to be close to zero, the ENM is likely to aggregate and adhere to soil particles, because the surface charges causing repulsion between particles are minimized.

Transport also explicitly depends on the size of the soil particles and the pore size. If the aggregate size is of similar dimensions or larger than the soil pore throats and is trapped, transport will likely be reduced by straining (Sirivithayapakorn and Keller 2003a, b), and by filtration if the particle is removed by interception, diffusion, and/or sedimentation (Bradford et al. 2002; Dunphy Guzman et al. 2006; Fang et al. 2009; Nowack and Bucheli 2007). As a result, it is possible that larger aggregates will be retained in the upper soil layers (Fang et al. 2009). The presence of clay particles and humic acid in soil can also cause adsorption of the ENMs if there are opposing surface charges between the ENMs and the surface mineral or organic deposits (Tourinho et al. 2012). Sorption can be caused by electrostatic attraction, surface bridging, hydrogen bonding, or hydrophobic interactions (Laak et al. 2006), which in turn are influenced by soil properties such as pH, metal oxide content, IS, organic fraction, and cation exchange capacity (Laak et al. 2006). However, if the ENM is similarly charged to the clay or NOM, such as nZVI coated with anionic hydrophilic carbon or poly-acrylic acid (PAA), both of which have anionic surface charges, transport through soil will be facilitated because the similar charge causes repulsion between the ENM and soil constituents (Schrick et al. 2004). Similarly, positively charged Al_2O_3 has little mobility and deposits rapidly in soils because the NPs sorb to the negatively charged soil particles. A phosphate coating on the Al_2O_3 , however, creates a negative charge and thus greater mobility (Darlington et al. 2009).

Much as in water, soil pH affects the aggregation of ENMs by altering surface charge, which strongly modulates ENM mobility in soils (Dunphy Guzman et al. 2006). For example, when the pH is near the point-of-zero-charge for both ZnO and TiO₂, transport is low (Godinez and Darnault 2011; Kanel et al. 2008). In one set of column experiments, a neutral pH prevented transport of TiO₂, whereas at most other pH values (such as 1, 10, and 12), 90–100 % of the TiO₂ NPs were transported the entire length of the soil column (Dunphy Guzman et al. 2006). This is also the case for Cu⁰ NPs, which are positively charged at a neutral pH and thus essentially immobile, whereas at high pH, surface charge becomes more negative, allowing transport by decreasing attachment efficiency (Jones and Su 2012).

IS can also affect the surface charge of ENMs; when IS is high it compresses the EDL, which decreases repulsive forces and mobility by increasing aggregation and sorption (Fang et al. 2009; Tourinho et al. 2012). For example, the presence of sodium chloride reduced the electrostatic repulsion between particles and soil for CuO, Fe₂O₃, latex, TiO₂, nZVI, and ZnO NPs, due to aggregation and reduced mobility (Ben-Moshe et al. 2010; Fang et al. 2009; Saleh et al. 2008a, b; Tufenkji and Elimelech 2004). Another study found that the compression of the EDL caused by increasing IS created a net attractive force for CeO₂, C₆₀, and MWCNTs NPs, which caused both increased aggregation and deposition (Brant et al. 2005; Li et al. 2011a, b, c; Tian et al. 2012). Similarly, studies with TiO₂ and ferrihydrite NPs indicated that mobility was high in low IS soils and low in high IS soils (Fang et al. 2009; Tosco et al. 2012).

Several studies have indicated that the electrolyte species matters significantly, much as it does in water (Espinasse et al. 2007; Jaisi and Elimelech 2009; Jaisi et al. 2008). For C₆₀, little aggregation occurred in the presence of NaCl, but significant aggregation occurred in the presence of CaCl₂, and mobility was equally affected by both (Wang et al. 2008a, b). Similarly deposition and filtration of C₆₀ and MWCNTs increase with increasing IS and also from monovalent to divalent cations (Espinasse et al. 2007; Jaisi et al. 2008). However, at high IS (>30 mM), the cation species effect can disappear and mobility will be minimal regardless of the electrolyte, such as for CNTs (Wang et al. 2008a, b). Thus, in groundwater that has traveled through calcareous deposits or with

increased salinity, ENM transport is likely to be significantly decreased. Similarly, in marine or estuarine sediments one would expect very limited mobility due to high attachment efficiencies to the sediments.

Much as in water, dissolved or particulate organic matter can sorb to ENM surfaces in soils, which can influence their fate in this medium. Soil organic matter may enhance the stability of ENMs and thus increase their mobility in soil (Ben-Moshe et al. 2010; Espinasse et al. 2007; Fang et al. 2009; Johnson et al. 2009). This is in part because humic substances tend to be negatively charged at typical environmental pH values, which can create an overall negative charge on an ENM-NOM agglomerate (Ghosh et al. 2008). For example, NOM in soil suspensions was found to have a stabilizing effect on TiO₂, nZVI, and SWCNTs, thus increasing their mobility (Arvidsson et al. 2011; Fang et al. 2009; Jaisi et al. 2008; Johnson et al. 2009). The presence of 2–20 mg L⁻¹ NOM greatly increased the mobility of nZVI over the absence of NOM (Johnson et al. 2009). NOM also decreased the attachment efficiency of both latex and Cu⁰ ENMs (Johnson et al. 2009; Jones and Su 2012; Tufenkji and Elimelech 2004). Similarly, deposition of TiO₂ was highest in the absence of NOM or bacteria and lowest in the presence of both NOM and bacteria, with NOM having a greater impact (Chowdhury et al. 2012). Under some conditions, however, the presence of NOM may destabilize particle dispersions (Tourinho et al. 2012). For example, the presence of polysaccharide-based natural organic matter, which is produced by algae or bacteria, may have the opposing effect to humic-based organic matter and thus may cause deposition and limit mobility (Espinasse et al. 2007).

Groundwater flow rate has also been shown to affect the mobility of ENMs (Tourinho et al. 2012). A low flow rate reduces ENM transport due to increased probability of collision, whereas a higher flow rate increases mobility in part due to the reduced likelihood of attachment (Ben-Moshe et al. 2010; Jeong and Kim 2009). For example, at the low flow velocity typical of groundwater (0.38 m/day), C₆₀ NPs showed limited mobility (Cheng et al. 2005). However, another study determined that while doubling the flow velocity did increase the transport of TiO₂, this increase was not significant (Godinez and Darnault 2011).

Transport estimates vary by NP and also by characteristics of the soil and flow. Thus, comparing

transport rates across very different experiments has limited use. Most studies show some transport for all ENMs. The longest transport was predicted for ferrihydrite (30 m) and functionalized fullerenes (10 m) (Lecoanet et al. 2004; Tosco et al. 2012). Silica is also expected to have a high mobility, in part because of the limited aggregation that occurs in soil (Lecoanet and Wiesner 2004). TiO₂ transport is expected to range from 41 to 370 cm, which may allow TiO₂ ENMs to reach deeper soil layers (Fang et al. 2009). SWCNTs are expected to experience some mobility in low IS soils (1.7 m), but transport could also be as low as 5–20 cm (Jaisi and Elimelech 2009; Jaisi et al. 2008). CNTs, MWCNTs, and Ag are expected to be relatively mobile, approximately to the same extent as natural clay colloids (Mattison et al. 2011; Tian et al. 2010). Al₂O₃ and uncoated nZVI, on the other hand, are expected to experience very little transport (Darlington et al. 2009; Jaisi and Elimelech 2009; Schrick et al. 2004). Transport can also be facilitated when NPs are attached to mobile clay particles, as seen for TiO₂, Ag, and Pu NPs (Abdel-Fattah et al. 2013; Zhou et al. 2012a).

These studies suggest that under some conditions, such as a neutral pH, high IS, low NOM, and low flow, many ENMs may have limited mobility and will be unlikely to enter deeply into groundwater aquifers or transport laterally to other water bodies (Brant et al. 2005). Conversely, in areas with high NOM or mobile clays, ENM transport may be significant during periods of saturation due to heavy rain. This is especially the case for ENMs that have coatings to make them less reactive, less likely to aggregate, and more mobile, such as functionalized fullerenes and CNTs, organically coated metal and metal oxide NPs, or iron-doped NPs, as well as certain other ENMs that are more stable, including TiO₂, silica, and Ag.

Toxicity

There is a growing body of literature on the toxicity of ENMs in many different systems. Most tests have been conducted on freshwater or marine species, with only a few on soil organisms. Toxic effects have been observed for many NPs at a range of concentrations, for a variety of species. Studies use various measures of toxicity including: no observed effect concentration (NOEC), minimum inhibitory concentration (MIC),

least observed effect concentration (LOEC), median lethal dose (LD50), median lethal concentration (LC50), half maximal effective concentration (EC50). For the purposes of this screening analysis, no distinction was made between chronic and acute toxicity, the particular toxic effect. As such, toxic effects could include direct death of individuals, limited growth rates, reproductive weaknesses, alterations to genetics, etc. The purpose of reviewing the literature on toxicity was to find the environmental concentrations at which any negative effect is caused to any species, so as to determine which ENMs are the greatest immediate threat at current production and predicted release concentrations.

In order to understand the risk of ENMs in the environment we must understand both the dose response effect of ENMs as well as the exposure pathway. Exposure pathway determines how an ENM enter an organism, which is generally via the respiratory system, the gastrointestinal system, or the epidermis (Davoren et al. 2007; Hoet et al. 2004; Li et al. 2007; Oberdörster et al. 2005; Warheit et al. 2004). Factors that may influence entry to an organism include ENM size, charge, surface area, and shape (Auffan et al. 2008; Yah et al. 2012). The morphology (i.e., spherical, cylindrical, etc.) of the ENM may be a significant determinant to the toxic response. For example, cylindrical carbon nanotubes have been found to act much like asbestos in the lungs of rats raising concerns that exposure may lead to pleural abnormalities such as mesothelioma, whereas other shapes of carbon-based nanoparticles such as fullerenes do not appear to be toxic (Oberdörster et al. 2005; Poland et al. 2008). Surface functionality also plays a role in determining the fate of nanomaterials, with hydrophilic Au NPs ingested and rapidly cleared with no toxic impact whereas hydrophobic NPs accumulated and caused toxicity in medaka (Zhu et al. 2010). Surface charge may also determine uptake, with greater uptake for positively charged NPs than neutral or negatively charged particles (Verma and Stellacci 2010; Zhu et al. 2010). The same was found for Au NPs where the cationic particles were moderately toxic, yet the anionic particles were non-toxic (Goodman et al. 2004). Surface coating and resulting charge determine toxicity for Ag NPs, with the most negatively charged citrate-capped Ag showed the least toxicity and the most positively charged polyethyleneimine (BPEI Ag NPs showing the most toxicity (El

Badawy et al. 2011). Surface coatings may also decrease toxicity by reducing ROS production. For example, oleic acid (OA) and poly(methylacrylic acid) (PMAA) coated ZnO NPs both reduced ROS production and cytotoxicity over uncoated ZnO NPs (Yin et al. 2010). Another study found that Ag NPs coated with protein were more toxic than those citrate-coated Ag NPs, which were more toxic than PVP-coated Ag NPs (Suresh et al. 2010). Toxicity will also depend on the persistence of ENMs within the organism or clearance from the organism due to an immune response (Card et al. 2008; Yah et al. 2012).

Once in an organism, ENMs may be able to transverse the cells and intermingle with tissue cells which can cause organ malfunction (Oberdörster et al. 2005). Cationic surfactant stabilized Au NPs were shown to readily transfer from the water column to an estuarine food web (Ferry et al. 2009). Studies have shown that airborne ENMs can be deposited in the respiratory tract when inhaled. From there, the NPs can transverse the blood stream, and be relocated to other organs (Warheit et al. 2004; Zhang et al. 2005). Gwinn and Vallyathan (2006) reported that inhaled nanosized particles may trigger phagocytosis and cause systemic health effects in experimental animals. ENMs can also enter an organism via the gastrointestinal tract through water, food, cosmetics, drugs, and medicines. TiO₂ ENMs have been found in the lymph, liver, and spleen after entry via the gastrointestinal tract (Jani et al. 1990). If exposure is via the epidermis, there is some possibility that SWCNTs and MWCNTs can enter cell membranes and cause oxidative stress and decreased viability based on in vitro studies (Manna et al. 2005).

Within an organism, ENMs appear to be transported to most major organs (Oberdörster et al. 2005). ENMs have proved toxic to human tissue and cell cultures, resulting in increased oxidative stress, inflammatory cytokine production and cell death (Oberdörster et al. 2005). Unlike larger particles, nanomaterials may be taken up by cell mitochondria and the cell nucleus (Geiser et al. 2005; Li et al. 2003; Porter et al. 2007). Studies demonstrate the potential for nanomaterials to cause DNA mutation and induce major structural damage to mitochondria, even resulting in cell death (Geiser et al. 2005; Li et al. 2003; Savić et al. 2003). Additionally, for ENMs with high mass to surface area ratios, the production of ROS can be quite high. ROS and free radical production may be

a significant mechanism of nanoparticle toxicity; it may result in oxidative stress, inflammation, and consequent damage to proteins, membranes, and DNA (Nel et al. 2006).

The results of 61 ENM ecotoxicity studies were placed into context by comparing them against the high end of current predicted release concentrations in freshwater and seawater media (Fig. 5), in order to estimate the level of risk an ENM poses in each media. Release concentration estimates for ENMs considered in this review range from the low ng L⁻¹ to µg L⁻¹

Freshwater	Seawater
SiO ₂	FeO/Fe ₂ O ₃ SWCNTs
Au FeO/Fe ₂ O ₃	Al ₂ O ₃ Cr ₂ O ₃ MWCNTs NiO TiO ₂
Al ₂ O ₃ CeO ₂ Cu CuO C ₆₀ Fe ₃ O ₄ Latex MWCNTs NiO SWCNTs TiO ₂	Au CeO ₂ CuO C ₆₀ SiO ₂
Ag nZVI ZnO	Ag nZVI ZnO

	No toxicity observed
	Toxic at >10 mg/L
	Toxic at <10 mg/L
	Toxic at 100x environmentally relevant concentrations

Fig. 5 Toxicity of ENMs in freshwater and marine systems. This table shows the highest toxicity thus measured for freshwater and seawater species

(Gottschalk et al. 2009; Keller and Lazareva 2013). There will likely be some hotspots and other exceptions, for instance where nZVI is directly injected into soil for groundwater remediation, or for accidental spills or improper disposal of ENMs outside of landfills. We grouped the risk of hazard, based on maximum predicted environmental concentrations and toxicity to the most sensitive species, into five categories: (1) toxic at maximum predicted environmental concentrations; (2) toxic at 100 times the maximum predicted environmental concentrations; (3) toxic at any concentration up to 10 mg L^{-1} ; (4) toxic at concentrations $>10 \text{ mg L}^{-1}$; and (5) non-toxic at all tested concentrations. The goal was to identify the most toxic concentration as yet identified in the literature and compare that with the current release estimates, which may change as more information becomes available. As new research is conducted, the location of some of these ENMs will likely shift in this table. Details for the studies considered in Fig. 5 are provided in Table S5.

At current predicted release quantities and using the results of current toxicity tests, none of the ENMs considered are expected to cause aquatic toxicity (Fig. 5). This is dependent on how and where the ENMs included in this study are released to surface waters (e.g., diffuse release vs. major spill). Even if current production and subsequent release quantities were to increase 100-fold, only three ENMs would raise concern: Ag, nZVI, and ZnO. Of these, ZnO is the greatest concern since all studies indicate ZnO is toxic at some concentration to all species tested (Blinova et al. 2010; Franklin et al. 2007; Li et al. 2013; Miller et al. 2010). If production of ZnO were to increase significantly, it is clear that its release and effects on the environment would need to be monitored closely. Also, special care should be given to the use of nZVI in soil and groundwater remediation as toxicity is observed at concentrations $>0.5\text{--}1 \text{ mg L}^{-1}$ (Keller et al. 2012), and typical remediation concentrations can range as high as $1\text{--}10 \text{ g/L}$ (Grieger et al. 2010; Phenrat et al. 2007). Additionally, while the production of Ag is currently quite low (Keller et al. 2013), most studies indicate some level of toxicity to a variety of species and thus consideration should be given should production increase. Toxicity from Ag may either be caused by the production of ROS or the interaction of Ag ions with thiol groups of vital

enzymes and proteins (Levard et al. 2012). However, the presence of sulfides in aquatic systems may limit toxicity by limiting the dissolution of Ag (Levard et al. 2011).

Carbon-based NPs, including C_{60} , SWCNTs, and MWCNTs show some toxicity at concentrations below 10 mg L^{-1} (Velzeboer et al. 2008; Zhu et al. 2007, 2009) and all other studies indicate some toxicity though not at concentrations likely to occur in the environment. Similarly, Cu/CuO, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$, and NiO also caused some toxicity at all tested concentrations. Some studies indicated toxicity at concentrations less than 10 mg L^{-1} (Aruoja et al. 2009; García et al. 2011; Griffitt et al. 2007, 2008; Heinlaan et al. 2008), while others indicated toxicity at far greater concentrations (e.g., Baek and An 2011; Blinova et al. 2010; Gong et al. 2011; Horie et al. 2009; Zhu et al. 2012).

Al_2O_3 , CeO_2 , and TiO_2 ENMs cause some toxicity at concentrations below 10 mg L^{-1} , and are clearly toxic at greater concentrations, although some studies indicated no toxicity at any tested concentration ranging from 25 mg L^{-1} to 20 g L^{-1} (e.g., Heinlaan et al. 2008; Jiang et al. 2009a, b; Miller et al. 2010; Velzeboer et al. 2008; Xia et al. 2008). Interestingly for CeO_2 , studies done on the same species and at similar concentrations occasionally resulted in toxic effects occurring at fairly different concentrations, which resulted in them being placed in different categories in this study (Gaiser et al. 2011; García et al. 2011; Hoecke et al. 2009; Rogers et al. 2010). A similar range of concentrations of TiO_2 caused differing toxic effects (e.g., Adams et al. 2006; García et al. 2011; Heinlaan et al. 2008; Simon-Deckers et al. 2009; Zhu et al. 2009).

Au, Cr_2O_3 , Sb_2O_3 , SiO_2 , and ZrO_2 ENMs exhibit very low toxicity, though fewer studies are available and as results are published their locations within the toxicity table may shift. Au caused toxicity only at 70 mg L^{-1} (Li et al. 2010a, b, c). Cr_2O_3 and ZrO_2 did not cause any toxicity at concentrations up to 100 mg L^{-1} (Horie et al. 2013; Singh et al. 2011; Velzeboer et al. 2008). Sb_2O_3 caused toxicity only at concentrations greater than 140 mg L^{-1} (Baek and An 2011). SiO_2 caused toxicity at very different concentrations for the same species; the lowest being 20 mg L^{-1} (Adams et al. 2006; Jiang et al. 2009a, b).

Most of these studies focused on toxicity of ENMs to aquatic organisms. A few, however, considered

toxicity to terrestrial organisms in soil. A number of studies have indicated toxicity of ENMs to soil organisms as well as the ability for ENMs such as Au and Ag to enter terrestrial food webs and biomagnify (Benn and Westerhoff 2008; Judy et al. 2011; Lowry et al. 2012a, b). At high exposure concentrations, reproduction of *E. fetida* decreased for both Au and Al₂O₃ (Coleman et al. 2010; Unrine et al. 2010). Along with harming reproduction in *E. fetida*, Ag was found to cause acute toxicity at 7.41 mg/kg in soil (Shoultz-Wilson et al. 2011). Both CuO and Fe₃O₄ were found to cause changes in soil microbial communities, caused by toxicity, at 1 and 5 % w/w dry soil (Ben-Moshe et al. 2013). Conversely C₆₀ caused no change in the functioning of microbial soil communities, even at very high concentrations, suggesting that toxicity may be strongly connected with bioavailability and thus solubility (Tong et al. 2007). While there are clearly toxic effects at both the acute and chronic level, specifically for bioavailable ENMs, there is virtually no information on actual exposure to ENMs in soils.

Conclusions

While there is still a need to better understand the implications of ENMs, emerging patterns with regards to ENM fate, transport, and exposure combined with emerging information on toxicity indicate that risk is low for most ENMs at predicted current environmental concentrations.

In the atmosphere, removal of ENMs will be via wet or dry deposition, both of which correlate strongly with particle size as well as environmental factors such as temperature, relative humidity, and atmospheric turbulence. A majority of ENMs are expected to settle very quickly due to interactions with larger particles, in spite of their small size. This will limit transport in the atmosphere.

The fate and transport of ENMs in natural waters is dependent on the characteristics of the ENM and the chemical properties of the water, specifically the IS and the presence of NOM and suspended particles. We found that there are clear differences in the fate of ENMs and the rate of ENM specific processes in different types of water, such as stormwater, freshwater, groundwater, and seawater.

Aggregation and sedimentation generally have similar time scales for most ENMs across the different water types. Faster aggregation indicates that NPs will not remain in the water column for long (residence times of hours to days) and thus exposure to many aquatic species will be limited, whereas slower aggregation, such as in stormwater or freshwater, may result in greater likelihood of exposure. Faster sedimentation (hours to days) generally indicates lowered exposure to species living in the water column, but increased and prolonged exposure to benthic species. Slower sedimentation (>weeks) indicates that ENMs will be transported over greater distances, but it may also mean greater dilution over time. ENMs will most likely exhibit low mobility in marine systems because of the higher rates of aggregation and sedimentation observed for many ENMs relative to freshwater. Areas near points of release (e.g., wastewater effluent discharge) may develop higher ENM concentrations in sediments over time, and may need to be monitored carefully for environmental impacts.

In most cases, dissolution does not vary significantly by water type, but is highly dependent on ENM composition. Ag, Al₂O₃, CuO, and NiO ENMs will dissolve over days to weeks, while ZnO dissolves even faster (hours to days). This will result in the release of metal ions and disappearance of the NP, although under some conditions the ENM may acquire a coating that slows down dissolution. The extent of oxidation and sulfidation, as well as interactions with phosphate and other ions, will also determine the extent of dissolution. Available data suggests that NPs that dissolve require close monitoring and merit more intensive follow-up research compared to those that do not dissolve. This is because, in many instances, the ionic form of a metal is very toxic and may have more significant effects than the NP. Frequently there is a strong correlation between toxicity and dissolution. The ENM may also be ingested by an organism and then dissolve, resulting in a high toxic dose. NPs that do not dissolve (e.g., SiO₂, TiO₂) tend to be much less toxic than those that do.

The fate of ENMs in soil is expected to be similar to those of traditional chemicals and colloids. For transport to occur, forces that cause ENMs to attach to soil particles must be minimized. In saturated soils the rates of aggregation, sedimentation, and dissolution are predictable based on their behavior in

groundwater. In unsaturated soils, work with colloids suggests that ENMs will be trapped at the air/water interface. The fate is strongly dependent on both primary particle size and aggregate particle size, as well as soil pore size, soil particle size, and soil characteristics. Under neutral pH, high IS (e.g., high salinity or hardness), low NOM, and low flow conditions, ENMs are unlikely to be transported great distances and are thus unlikely to enter groundwater aquifers to a significant depth. This information can be used to design ENM removal mechanisms in soil applications.

More research must be conducted on rates of heteroaggregation and sedimentation in complex aquatic media and at environmentally realistic concentrations. Most studies included in this paper were conducted at mg/L concentrations, which cannot in all cases be scaled down to the far more likely ng/L or $\mu\text{g/L}$ concentrations that are likely present in the environment. Most studies on aggregation, sorption, sedimentation, and dissolution use simplified aquatic or soil media, which makes it far more difficult to predict actual rates of transformation processes in the environment. In particular, quantitative changes in concentration over time and transport in soils are often not reported; these are necessary to both quantify fate and transport and to be able to compare across types of nanomaterials. Additionally, more work should be done on the rate and extent of transformation and reactions with other ions and complex NOM that occur in the environment. Results of studies should also be presented in a standardized quantitative manner so that they can be compared statistically across various ENM types, sizes, and shapes and environments.

Toxicity is not expected at current predicted environmental concentrations for the ENMs considered in this study. It is important to note that predicted environmental concentrations have a high degree of uncertainty, and thus the assessment should adapt as more information becomes available. However, direct use of ENMs in the environment (e.g., nZVI) or spills and other direct releases may have significant local effects. Even if current production and release were to increase 100-fold, only Ag, nZVI, and ZnO would be of significant concern. Generally, toxicity was highest for Ag, CuO, NiO, nZVI, and ZnO, as expected based on their dissolution behavior. Additionally, while fewer studies have been conducted on the toxicity of ENMs to soil organisms, in part because of the

complexity with which organisms are exposed to ENMs in the different soil phases, studies do indicate that ENMs such as Ag, Au, Al_2O_3 , CuO, and Fe_3O_4 will cause toxicity if ENM concentrations in soil become high enough.

The results from these 61 toxicity studies, combined with emerging exposure predictions, indicate that there are some areas of concern. ENMs such as Ag, nZVI, and ZnO are all relatively well studied and may pose risks under some release scenarios. After these, research should be directed toward the possible effects of C-based NPs, Cu ENMs, Fe ENMs, and NiO since all will cause toxicity but only if production and release quantities increase by several orders of magnitude. In addition, because Al_2O_3 and TiO_2 both have high production levels that are likely to increase, their risk should be carefully evaluated as well.

References

- Abdel-Fattah AI, Zhou D, Boukhalfa H, Tarimala S, Ware SD, Keller AA (2013) Dispersion stability and electrokinetic properties of intrinsic plutonium colloids: implications for subsurface transport. *Environ Sci Technol* 47(11):5626–5634
- Adams LK, Lyon DY, Alvarez PJJ (2006) Comparative ecotoxicity of nanoscale TiO_2 , SiO_2 , and ZnO water suspensions. *Water Res* 40(19):3527–3532
- Adeleye AS, Keller AA (2014) Long-term colloidal stability and metal leaching of single wall carbon nanotubes: effect of temperature and extracellular polymeric substances. *Water Res* 49:236–250
- Adeleye AS, Keller AA, Miller RJ, Lenihan HS (2013) Persistence of commercial nanoscaled zero-valent iron (nZVI) and by-products. *J Nanopart Res* 15(1):1–18
- Allen HE, Hansen DJ (1996) The importance of trace metal speciation to water quality criteria. *Water Environ Res* 68(1):42–54
- Aruoja V, Dubourguier H-C, Kasemets K, Kahru A (2009) Toxicity of nanoparticles of CuO, ZnO and TiO_2 to microalgae *Pseudokirchneriella subcapitata*. *Sci Total Environ* 407(4):1461–1468
- Arvidsson R, Molander S, Sandén BA, Hassellöv M (2011) Challenges in exposure modeling of nanoparticles in aquatic environments. *Hum Ecol Risk Assess Int J* 17(1):245–262
- Auffan M, Achouak W, Rose J, Roncato M-A, Chanéac C, Waite DT, Masion A et al (2008) Relation between the redox state of iron-based nanoparticles and their cytotoxicity toward *Escherichia coli*. *Environ Sci Technol* 42(17):6730–6735
- Baalousha M (2009) Aggregation and disaggregation of iron oxide nanoparticles: influence of particle concentration, pH and natural organic matter. *Sci Total Environ* 407(6):2093–2101

- Baalousha M, Manciuola A, Cumberland S, Kendall K, Lead JR (2008) Aggregation and surface properties of iron oxide nanoparticles: influence of pH and natural organic matter. *Environ Toxicol Chem* 27(9):1875–1882
- Badawy AME, Luxton TP, Silva RG, Scheckel KG, Suidan MT, Tolaymat TM (2010) Impact of environmental conditions (pH, ionic strength, and electrolyte type) on the surface charge and aggregation of silver nanoparticles suspensions. *Environ Sci Technol* 44(4):1260–1266
- Baek YW, An YJ (2011) Microbial toxicity of metal oxide nanoparticles (CuO, NiO, ZnO, and Sb₂O₃) to *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus aureus*. *Sci Total Environ* 409(8):1603–1608
- Baumgartner H, Loeffler F (1986) Experimental and theoretical investigation of the time-dependent collection performance of electret filters. pp 708–711
- Bello D, Wardle BL, Yamamoto N, deVilloria RG, Garcia EJ, Hart AJ, Ahn K et al (2009) Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes. *J Nanopart Res* 11(1):231–249
- Ben-Moshe T, Dror I, Berkowitz B (2010) Transport of metal oxide nanoparticles in saturated porous media. *Chemosphere* 81(3):387–393
- Ben-Moshe T, Frenk S, Dror I, Minz D, Berkowitz B (2013) Effects of metal oxide nanoparticles on soil properties. *Chemosphere* 90(2):640–646
- Benn TM, Westerhoff P (2008) Nanoparticle silver released into water from commercially available sock fabrics. *Environ Sci Technol* 42(11):4133–4139
- Bennett SW, Adeleye A, Ji Z, Keller AA (2013) Stability, metal leaching, photoactivity and toxicity in freshwater systems of commercial single wall carbon nanotubes. *Water Res* 47(12):4074–4085
- Blaser SA, Scheringer M, MacLeod M, Hungerbühler K (2008) Estimation of cumulative aquatic exposure and risk due to silver: contribution of nano-functionalized plastics and textiles. *Sci Total Environ* 390(2–3):396–409
- Blinova I, Ivask A, Heinlaan M, Mortimer M, Kahru A (2010) Ecotoxicity of nanoparticles of CuO and ZnO in natural water. *Environ Pollut* 158(1):41–47
- Bondarenko O, Juganson K, Ivask A, Kasemets K, Mortimer M, Kahru A (2013) Toxicity of Ag, CuO and ZnO nanoparticles to selected environmentally relevant test organisms and mammalian cells in vitro: a critical review. *Arch Toxicol* 87(7):1181–1200
- Bradford SA, Yates SR, Bettahar M, Simunek J (2002) Physical factors affecting the transport and fate of colloids in saturated porous media. *Water Resour Res* 38(12):1327
- Brant J, Lecoanet H, Wiesner MR (2005) Aggregation and deposition characteristics of fullerene nanoparticles in aqueous systems. *J Nanopart Res* 7(4–5):545–553
- Brouwer D (2010) Exposure to manufactured nanoparticles in different workplaces. *Toxicology* 269(2–3):120–127
- Brouwer D, Duuren-Stuurman B, van Berges M, Jankowska E, Jankowska E, Bard D, Mark D (2009) From workplace air measurement results toward estimates of exposure? Development of a strategy to assess exposure to manufactured nano-objects. *J Nanoparticle Res* 11(8):1867–1881
- Cabot A, Smith RK, Yin Y, Zheng H, Reinhard BM, Liu H, Alivisatos AP (2008) Sulfidation of cadmium at the nanoscale. *ACS Nano* 2(7):1452–1458
- Card JW, Zeldin DC, Bonner JC, Nestmann ER (2008) Pulmonary applications and toxicity of engineered nanoparticles. *Am J Physiol Lung Cell Mol Physiol* 295(3):L400–L411
- Chang MCO, Chow JC, Watson JG, Hopke PK, Yi S-M, England GC (2004) Measurement of ultrafine particle size distributions from coal-, oil-, and gas-fired stationary combustion sources. *J Air Waste Manag Assoc* 54(12):1494–1505
- Chen KL, Elimelech M (2007) Influence of humic acid on the aggregation kinetics of fullerene (C₆₀) nanoparticles in monovalent and divalent electrolyte solutions. *J Colloid Interface Sci* 309(1):126–134
- Chen KL, Mylon SE, Elimelech M (2006) Aggregation kinetics of alginate-coated hematite nanoparticles in monovalent and divalent electrolytes. *Environ Sci Technol* 40(5):1516–1523
- Chen KL, Mylon SE, Elimelech M (2007) Enhanced aggregation of alginate-coated iron oxide (hematite) nanoparticles in the presence of calcium, strontium, and barium cations. *Langmuir* 23(11):5920–5928
- Cheng X, Kan AT, Tomson MB (2005) Study of C₆₀ transport in porous media and the effect of sorbed C₆₀ on naphthalene transport. *J Mater Res* 20(12):3244–3254
- Chinnapongse SL, MacCuspie RI, Hackley VA (2011) Persistence of singly dispersed silver nanoparticles in natural freshwaters, synthetic seawater, and simulated estuarine waters. *Sci Total Environ* 409(12):2443–2450
- Chowdhury I, Cwiertny DM, Walker SL (2012) Combined factors influencing the aggregation and deposition of nano-TiO₂ in the presence of humic acid and bacteria. *Environ Sci Technol* 46(13):6968–6976
- Christian P, der Kammer FV, Baalousha M, Hofmann T (2008) Nanoparticles: structure, properties, preparation and behaviour in environmental media. *Ecotoxicology* 17(5):326–343
- Coleman JG, Johnson DR, Stanley JK, Bednar AJ, Weiss CA, Boyd RE, Steevens JA (2010) Assessing the fate and effects of nano aluminum oxide in the terrestrial earthworm, *Eisenia fetida*. *Environ Toxicol Chem* 29(7):1575–1580
- Cornelis G, Ryan B, McLaughlin MJ, Kirby JK, Beak D, Chittleborough D (2011) Solubility and batch retention of CeO₂ nanoparticles in soils. *Environ Sci Technol* 45(7):2777–2782
- Curwin B, Bertke S (2011) Exposure characterization of metal oxide nanoparticles in the workplace. *J Occup Environ Hyg* 8(10):580–587
- Daou TJ, Begin-Colin S, Grenèche JM, Thomas F, Derory A, Bernhardt P, Legaré P et al (2007) Phosphate adsorption properties of magnetite-based nanoparticles. *Chem Mater* 19(18):4494–4505
- Darlington TK, Neigh AM, Spencer MT, Guyen OTN, Oldenburg SJ (2009) Nanoparticle characteristics affecting environmental fate and transport through soil. *Environ Toxicol Chem* 28(6):1191–1199
- Davoren M, Herzog E, Casey A, Cottineau B, Chambers G, Byrne HJ, Lyng FM (2007) In vitro toxicity evaluation of

- single walled carbon nanotubes on human A549 lung cells. *Toxicol Vitro Int J Publ Assoc BIBRA* 21(3):438–448
- Delay M, Dolt T, Woellhaf A, Sembritzki R, Frimmel FH (2011) Interactions and stability of silver nanoparticles in the aqueous phase: influence of natural organic matter (NOM) and ionic strength. *J Chromatogr A* 1218(27):4206–4212
- Dunphy Guzman KA, Finnegan MP, Banfield JF (2006) Influence of surface potential on aggregation and transport of titania nanoparticles. *Environ Sci Technol* 40(24):7688–7693
- El Badawy AM, Silva RG, Morris B, Scheckel KG, Suidan MT, Tolaymat TM (2011) Surface charge-dependent toxicity of silver nanoparticles. *Environ Sci Technol* 45(1):283–287
- Elimelech M, Jia X, Gregory J, Williams R (1998) Particle deposition and aggregation: measurement, modeling, and simulation. Butterworth-Heinemann, Oxford
- Elzey S, Grassian V (2010) Agglomeration, isolation and dissolution of commercially manufactured silver nanoparticles in aqueous environments. *J Nanopart Res* 12(5):1945–1958
- Espinasse B, Hotze EM, Wiesner MR (2007) Transport and retention of colloidal aggregates of c60 in porous media: effects of organic macromolecules, ionic composition, and preparation method. *Environ Sci Technol* 41(21):7396–7402
- Fabrega J, Fawcett SR, Renshaw JC, Lead JR (2009) Silver nanoparticle impact on bacterial growth: effect of pH, concentration, and organic matter. *Environ Sci Technol* 43(19):7285–7290
- Fairbairn EA, Keller AA, Mädler L, Zhou D, Pokhrel S, Cherr GN (2011) Metal oxide nanomaterials in seawater: linking physicochemical characteristics with biological response in sea urchin development. *J Hazard Mater* 192(3):1565–1571
- Fang J, Shan X, Wen B, Lin J, Owens G (2009) Stability of titania nanoparticles in soil suspensions and transport in saturated homogeneous soil columns. *Environ Pollut* 157(4):1101–1109
- Feitz AJ, Joo SH, Guan J, Sun Q, Sedlak DL, David Waite T (2005) Oxidative transformation of contaminants using colloidal zero-valent iron. *Colloids Surf Physicochem Eng Asp* 265(1–3):88–94
- Ferry JL, Craig P, Hexel C, Sisco P, Frey R, Pennington PL, Fulton MH, Scott GI, Decho AW, Kashiwada S, Murphy CJ, Saw TJ (2009) Transfer of gold nanoparticles from the water column to the estuarine food web. *Nat Nanotechnol* 4(7):441–444
- Flemming CA, Trevors JT (1989) Copper toxicity and chemistry in the environment: a review. *Water Air Soil Pollut* 44(1–2):143–158
- Fortner JD, Lyon DY, Sayes CM, Boyd AM, Falkner JC, Hotze EM, Alemany LB, Tao YJ, Guo W, Ausman KD, Colvin VL, Hughes JB (2005) C60 in water: nanocrystal formation and microbial response. *Environ Sci Technol* 39(11):4307–4316
- Franklin NM, Rogers NJ, Apte SC, Batley GE, Gadd GE, Casey PS (2007) Comparative toxicity of nanoparticulate ZnO, bulk ZnO, and ZnCl₂ to a freshwater microalga (*Pseudokirchneriella subcapitata*): the importance of particle solubility. *Environ Sci Technol* 41(24):8484–8490
- French RA, Jacobson AR, Kim B, Isley SL, Penn RL, Baveye PC (2009) Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles. *Environ Sci Technol* 43(5):1354–1359
- Friedlander SK, Pui DYH (2004) Emerging issues in nanoparticle aerosol science and technology. *J Nanopart Res* 6(2):313–320
- Fujitani Y, Kobayashi T, Arashidani K, Kunugita N, Suemura K (2008) Measurement of the physical properties of aerosols in a fullerene factory for inhalation exposure assessment. *J Occup Environ Hyg* 5(6):380–389
- Gaiser BK, Biswas A, Rosenkranz P, Jepson MA, Lead JR, Stone V, Tyler CR, Fernandes TF (2011) Effects of silver and cerium dioxide micro- and nano-sized particles on *Daphnia magna*. *J Environ Monit* 13(5):1227
- García A, Espinosa R, Delgado L, Casals E, González E, Puentes V, Barata C, Font C, Sanchez A (2011) Acute toxicity of cerium oxide, titanium oxide and iron oxide nanoparticles using standardized tests. *Desalination* 269(1–3):136–141
- Geiser M, Rothen-Rutishauser B, Kapp N, Schurch S, Kreyling W, Schulz H, Semmler M et al (2005) Ultrafine particles cross cellular membranes by nonphagocytic mechanisms in lungs and in cultured cells. *Environ Health Perspect* 113(11):1555–1560
- Ghosh S, Mashayekhi H, Pan B, Bhowmik P, Xing B (2008) Colloidal behavior of aluminum oxide nanoparticles as affected by pH and natural organic matter. *Langmuir* 24(21):12385–12391
- Ghosh S, Mashayekhi H, Bhowmik P, Xing B (2010) Colloidal stability of Al₂O₃ nanoparticles as affected by coating of structurally different humic acids. *Langmuir* 26(2):873–879
- Gilbert B, Lu G, Kim CS (2007) Stable cluster formation in aqueous suspensions of iron oxyhydroxide nanoparticles. *J Colloid Interface Sci* 313(1):152–159
- Godinez IG, Darnault CJG (2011) Aggregation and transport of nano-TiO₂ in saturated porous media: effects of pH, surfactants and flow velocity. *Water Res* 45(2):839–851
- Gong L, Xu B, Zhu Y (2009) Ultrafine particles deposition inside passenger vehicles. *Aerosol Sci Technol* 43(6):544–553
- Gong N, Shao K, Feng W, Lin Z, Liang C, Sun Y (2011) Biotoxicity of nickel oxide nanoparticles and bio-remediation by microalgae *Chlorella vulgaris*. *Chemosphere* 83(4):510–516
- Goodman CM, McCusker CD, Yilmaz T, Rotello VM (2004) Toxicity of gold nanoparticles functionalized with cationic and anionic side chains. *Bioconjug Chem* 15(4):897–900
- Gottschalk F, Sonderer T, Scholz RW, Nowack B (2009) Modeled environmental concentrations of engineered nanomaterials (TiO₂, ZnO, Ag, CNT, fullerenes) for different regions. *Environ Sci Technol* 43(24):9216–9222
- Gottschalk F, Scholz RW, Nowack B (2010) Probabilistic material flow modeling for assessing the environmental exposure to compounds: methodology and an application to engineered nano-TiO₂ particles. *Environ Model Softw* 25(3):320–332
- Gottschalk F, Ort C, Scholz RW, Nowack B (2011) Engineered nanomaterials in rivers—exposure scenarios for Switzerland at high spatial and temporal resolution. *Environ Pollut* 159(12):3439–3445
- Grieger KD, Fjordbøge A, Hartmann NB, Eriksson E, Bjerg PL, Baun A (2010) Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off? *J Contam Hydrol* 118(3–4):165–183

- Griffitt RJ, Weil R, Hyndman KA, Denslow ND, Powers K, Taylor D, Barber DS (2007) Exposure to copper nanoparticles causes gill injury and acute lethality in zebrafish (*Danio rerio*). *Environ Sci Technol* 41(23):8178–8186
- Griffitt RJ, Luo J, Gao J, Bonzongo JC, Barber DS (2008) Effects of particle composition and species on toxicity of metallic nanomaterials in aquatic organisms. *Environ Toxicol Chem* 27(9):1972–1978
- Gwinn MR, Vallyathan V (2006) Nanoparticles: health effects—pros and cons. *Environ Health Perspect* 114(12):1818–1825
- Hammes J, Gallego-Urrea JA, Hassellöv M (2013) Geographically distributed classification of surface water chemical parameters influencing fate and behavior of nanoparticles and colloid facilitated contaminant transport. *Water Res* 47(14):5350–5361
- Handy R, von der Kammer F, Lead J, Hassellöv M, Owen R, Crane M (2008) The ecotoxicology and chemistry of manufactured nanoparticles. *Ecotoxicology* 17(4):287–314
- Heinlaan M, Ivask A, Blinova I, Dubourguier HC, Kahru A (2008) Toxicity of nanosized and bulk ZnO, CuO and TiO₂ to bacteria *Vibrio fischeri* and crustaceans *Daphnia magna* and *Thamnocephalus platyurus*. *Chemosphere* 71(7):1308–1316
- Hendren CO, Lowry M, Grieger KD, Money ES, Johnston JM, Wiesner MR, Beaulieu SM (2013) Modeling approaches for characterizing and evaluating environmental exposure to engineered nanomaterials in support of risk-based decision making. *Environ Sci Technol* 47(3):1190–1205
- Hennebert P, Avellan A, Yan J, Aguerre-Chariol O (2013) Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. *Waste Manag* 33(9):1870–1881
- Hitchman A, Sambrook Smith GH, Ju-Nam Y, Sterling M, Lead JR (2013) The effect of environmentally relevant conditions on PVP stabilised gold nanoparticles. *Chemosphere* 90(2):410–416
- Hoecke KV, Quik JTK, Mankiewicz-Boczek J, Schampelaere KACD, Elsaesser A, der Meeren PV, Barnes C, Howard CV, Meent DVD, Rydzynski K, Dawson KA, Salvati A, Lesniak A, Silversmit G, Samber BD, Vincze L, Janssen CR (2009) Fate and effects of CeO₂ nanoparticles in aquatic ecotoxicity tests. *Environ Sci Technol* 43(12):4537–4546
- Hoet PH, Brüske-Hohlfeld I, Salata OV (2004) Nanoparticles—known and unknown health risks. *J Nanobiotechnol* 2(1):12
- Horie M, Nishio K, Fujita K, Kato H, Nakamura A, Kinugasa S, Endoh S, Miyauchi A, Yamamoto K, Murayama H, Niki E, Iwahashi H, Nakanishi J (2009) Ultrafine NiO particles induce cytotoxicity in vitro by cellular uptake and subsequent Ni(II) release. *Chem Res Toxicol* 22(8):1415–1426
- Horie M, Nishio K, Endoh S, Kato H, Fujita K, Miyauchi A, Nakamura A, Kinugasa S, Yamamoto K, Niki E, Yoshida Y, Iwahashi H (2013) Chromium(III) oxide nanoparticles induced remarkable oxidative stress and apoptosis on culture cells. *Environ Toxicol* 28(2):61–75
- Hyung H, Kim J-H (2008) Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: effect of NOM characteristics and water quality parameters. *Environ Sci Technol* 42(12):4416–4421
- Illés E, Tombác E (2006) The effect of humic acid adsorption on pH-dependent surface charging and aggregation of magnetite nanoparticles. *J Colloid Interface Sci* 295(1):115–123
- Isrealachvili JN (1992) Intermolecular and surface forces, 2nd edn. Academic Press, London
- Jacobson MZ (2003) Development of mixed-phase clouds from multiple aerosol size distributions and the effect of the clouds on aerosol removal. *J Geophys Res Atmos* 108(D8):4245
- Jaisi DP, Elimelech M (2009) Single-walled carbon nanotubes exhibit limited transport in soil columns. *Environ Sci Technol* 43(24):9161–9166
- Jaisi DP, Saleh NB, Blake RE, Elimelech M (2008) Transport of single-walled carbon nanotubes in porous media: filtration mechanisms and reversibility. *Environ Sci Technol* 42(22):8317–8323
- Jana NR, Earhart C, Ying JY (2007) Synthesis of water-soluble and functionalized nanoparticles by silica coating. *Chem Mater* 19(21):5074–5082
- Jani P, Halbert GW, Langridge J, Florence AT (1990) Nanoparticle uptake by the rat gastrointestinal mucosa: quantitation and particle size dependency. *J Pharm Pharmacol* 42(12):821–826
- Jeong SW, Kim SD (2009) Aggregation and transport of copper oxide nanoparticles in porous media. *J Environ Monit* 11(9):1595
- Jeong CH, Hopke PK, Chalupa D, Utell M (2004) Characteristics of nucleation and growth events of ultrafine particles measured in Rochester, NY. *Environ Sci Technol* 38(7):1933–1940
- Jiang J, Oberdörster G, Biswas P (2009a) Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies. *J Nanopart Res* 11(1):77–89
- Jiang W, Mashayekhi H, Xing B (2009b) Bacterial toxicity comparison between nano- and micro-scaled oxide particles. *Environ Pollut* 157(5):1619–1625
- Johnson RL, Johnson GO, Nurmi JT, Tratnyek PG (2009) Natural organic matter enhanced mobility of nano zero-valent iron. *Environ Sci Technol* 43(14):5455–5460
- Johnston J, Lowry M, Beaulieu S, Bowles E (2010) State-of-the-science report on predictive models and modeling approaches for characterizing and evaluating exposure to nanomaterials. National Exposure Research Laboratory. http://www.epa.gov/athens/publications/reports/Johnston_EPA600R10129_State_of_Science_Predictive_Models.pdf. Accessed 2 Jan 2014
- Jones EH, Su C (2012) Fate and transport of elemental copper (Cu₀) nanoparticles through saturated porous media in the presence of organic materials. *Water Res* 46(7):2445–2456
- Joo SH, Zhao D (2008) Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: effects of catalyst and stabilizer. *Chemosphere* 70(3):418–425
- Joo SH, Feitz AJ, Waite TD (2004) Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. *Environ Sci Technol* 38(7):2242–2247
- Judy JD, Unrine JM, Bertsch PM (2011) Evidence for biomagnification of gold nanoparticles within a terrestrial food chain. *Environ Sci Technol* 45(2):776–781

- Kandah MI (2004) Zinc and cadmium adsorption on low-grade phosphate. *Sep Purif Technol* 35(1):61–70
- Kanel SR, Goswami RR, Clement TP, Barnett MO, Zhao D (2008) Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media. *Environ Sci Technol* 42(3):896–900
- Keller AA, Lazareva A (2013) Predicted releases of engineered nanomaterials: from global to regional to local. *Environ Sci Technol Lett* 2013:65–70
- Keller AA, Wang H, Zhou D, Lenihan HS, Cherr G, Cardinale BJ, Miller R, Ji Z (2010) Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environ Sci Technol* 44(6):1962–1967
- Keller AA, Garner K, Miller RJ, Lenihan HS (2012) Toxicity of nano-zero valent iron to freshwater and marine organisms. *PLoS One* 7(8):e43983
- Keller AA, McFerran S, Lazareva A, Suh S (2013) Global life cycle releases of engineered nanomaterials. *J Nanopart Res* 15(6):1–17
- Kim H-J, Phenrat T, Tilton RD, Lowry GV (2009) Fe⁰ nanoparticles remain mobile in porous media after aging due to slow desorption of polymeric surface modifiers. *Environ Sci Technol* 43(10):3824–3830
- Kim B, Park C-S, Murayama M, Hochella MF (2010) Discovery and characterization of silver sulfide nanoparticles in final sewage sludge products. *Environ Sci Technol* 44(19):7509–7514
- Kiser MA, Westerhoff P, Benn T, Wang Y, Pérez-Rivera J, Hristovski K (2009) Titanium nanomaterial removal and release from wastewater treatment plants. *Environ Sci Technol* 43(17):6757–6763
- Klaine SJ, Alvarez PJJ, Batley GE, Fernandes TF, Handy RD, Lyon DY, Mahendra S, McLaughlin MJ, Lead JR (2008) Nanomaterials in the environment: behavior, fate, bio-availability, and effects. *Environ Toxicol Chem* 27(9):1825–1851
- Kuhlbusch TA, Asbach C, Fissan H, Göhler D, Stintz M (2011) Nanoparticle exposure at nanotechnology workplaces: a review. *Part Fibre Toxicol* 8(1):22
- Kumar P, Ketzler M, Vardoulakis S, Pirjola L, Britter R (2011) Dynamics and dispersion modelling of nanoparticles from road traffic in the urban atmospheric environment—a review. *J Aerosol Sci* 42(9):580–603
- Kvitek L, Panacek A, Soukupova J, Kolar M, Vecerova R, Prucek R, Holecova M et al (2008) Effect of surfactants and polymers on stability and antibacterial activity of silver nanoparticles (NPs). *J Phys Chem C* 112(15):5825–5834
- Laakso L, Grönholm T, Rannik Ü, Kosmale M, Fiedler V, Vehkamäki H, Kulmala M (2003) Ultrafine particle scavenging coefficients calculated from 6 years field measurements. *Atmos Environ* 37(25):3605–3613
- Lecoanet HF, Wiesner MR (2004) Velocity effects on fullerene and oxide nanoparticle deposition in porous media. *Environ Sci Technol* 38(16):4377–4382
- Lecoanet HF, Bottero JY, Wiesner MR (2004) Laboratory assessment of the mobility of nanomaterials in porous media. *Environ Sci Technol* 38(19):5164–5169
- Lee JH, Ahn K, Kim SM, Jeon KS, Lee JS, Yu IJ (2012) Continuous 3-day exposure assessment of workplace manufacturing silver nanoparticles. *J Nanopart Res* 14(9):1–10
- Levard C, Reinsch BC, Michel FM, Oumahi C, Lowry GV, Brown GE (2011) Sulfidation processes of PVP-coated silver nanoparticles in aqueous solution: impact on dissolution rate. *Environ Sci Technol* 45(12):5260–5266
- Levard C, Hotze EM, Lowry GV, Brown GE (2012) Environmental transformations of silver nanoparticles: impact on stability and toxicity. *Environ Sci Technol* 46(13):6900–6914
- Li N, Sioutas C, Cho A, Schmitz D, Misra C, Sempf J, Wang M et al (2003) Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ Health Perspect* 111(4):455–460
- Li Z, Hulderman T, Salmen R, Chapman R, Leonard SS, Young S-H, Shvedova A et al (2007) Cardiovascular effects of pulmonary exposure to single-wall carbon nanotubes. *Environ Health Perspect* 115(3):377–382
- Li T, Albee B, Alemayehu M, Diaz R, Ingham L, Kamal S, Rodriguez M, Bishnoi SW (2010a) Comparative toxicity study of Ag, Au, and Ag–Au bimetallic nanoparticles on *Daphnia magna*. *Anal Bioanal Chem* 398(2):689–700
- Li X, Lenhart JJ, Walker HW (2010b) Dissolution-accompanied aggregation kinetics of silver nanoparticles. *Langmuir* 26(22):16690–16698
- Li Z, Greden K, Alvarez PJJ, Gregory KB, Lowry GV (2010c) Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zerovalent iron to *E. coli*. *Environ Sci Technol* 44(9):3462–3467
- Li M, Zhu L, Lin D (2011a) Toxicity of ZnO nanoparticles to *Escherichia coli*: mechanism and the influence of medium components. *Environ Sci Technol* 45(5):1977–1983
- Li X, Lenhart JJ, Walker HW (2011b) Aggregation kinetics and dissolution of coated silver nanoparticles. *Langmuir* 28(2):1095–1104
- Li Z, Sahle-Demessie E, Hassan AA, Sorial GA (2011c) Transport and deposition of CeO₂ nanoparticles in water-saturated porous media. *Water Res* 45(15):4409–4418
- Li M, Lin D, Zhu L (2013) Effects of water chemistry on the dissolution of ZnO nanoparticles and their toxicity to *Escherichia coli*. *Environ Pollut* 173:97–102
- Liu HH, Cohen Y (2014) Multimedia environmental distribution of engineered nanomaterials. *Environ Sci Technol* 48(6):3281–3292
- Liu J, Pennell KG, Hurt RH (2011) Kinetics and mechanisms of nanosilver oxysulfidation. *Environ Sci Technol* 45(17):7345–7353
- Liu J, von der Kammer F, Zhang B, Legros S, Hofmann T (2013a) Combining spatially resolved hydrochemical data with in vitro nanoparticle stability testing: assessing environmental behavior of functionalized gold nanoparticles on a continental scale. *Environ Int* 59:53–62
- Liu X, Chen G, Erwin JG, Adam NK, Su C (2013b) Release of phosphorous impurity from TiO₂ anatase and rutile nanoparticles in aquatic environments and its implications. *Water Res* 47(16):6149–6156
- Lowry GV, Espinasse BP, Badireddy AR, Richardson CJ, Reinsch BC, Bryant LD, Bone AJ, Deonaraine A, Chae S, Therezien M, Colman BP, Hsu-Kim H, Bernhardt ES, Matson CW, Wiesner MR (2012a) Long-term transformation and fate of manufactured Ag nanoparticles in a simulated large scale freshwater emergent wetland. *Environ Sci Technol* 46(13):7027–7036
- Lowry GV, Gregory KB, Apte SC, Lead JR (2012b) Transformations of nanomaterials in the environment. *Environ Sci Technol* 46(13):6893–6899

- Luther GW III, Tsamakis E (1989) Concentration and form of dissolved sulfide in theoxic water column of the ocean. *Mar Chem* 27(3–4):165–177
- Lv J, Zhang S, Luo L, Han W, Zhang J, Yang K, Christie P (2012) Dissolution and microstructural transformation of ZnO nanoparticles under the influence of phosphate. *Environ Sci Technol* 46(13):7215–7221
- Ma R, Levard C, Marinakos SM, Cheng Y, Liu J, Michel FM, Brown GE et al (2012) Size-controlled dissolution of organic-coated silver nanoparticles. *Environ Sci Technol* 46(2):752–759
- Ma R, Levard C, Michel FM, Brown GE, Lowry GV (2013) Sulfidation mechanism for zinc oxide nanoparticles and the effect of sulfidation on their solubility. *Environ Sci Technol* 47(6):2527–2534
- Ma R, Levard C, Judy JD, Unrine JM, Durenkamp M, Martin B, Jefferson B et al (2014) Fate of zinc oxide and silver nanoparticles in a pilot wastewater treatment plant and in processed biosolids. *Environ Sci Technol* 48(1):104–112
- Mackay D, Paterson S, Shiu WY (1992) Generic models for evaluating the regional fate of chemicals. *Chemosphere* 24(6):695–717
- Manna SK, Sarkar S, Barr J, Wise K, Barrera EV, Jejelowo O, Rice-Ficht AC et al (2005) Single-walled carbon nanotube induces oxidative stress and activates nuclear transcription factor- κ B in human keratinocytes. *Nano Lett* 5(9):1676–1684
- Mattison NT, O'Carroll DM, Kerry Rowe R, Petersen EJ (2011) Impact of porous media grain size on the transport of multi-walled carbon nanotubes. *Environ Sci Technol* 45(22):9765–9775
- Maynard AD, Zimmer AT (2003) Development and validation of a simple numerical model for estimating workplace aerosol size distribution evolution through coagulation, settling, and diffusion. *Aerosol Sci Technol* 37(10):804–817
- Meesters JA, Veltman K, Hendriks AJ, van de Meent D (2013) Environmental exposure assessment of engineered nanoparticles: why REACH needs adjustment. *Integr Environ Assess Manag* 9(3):e15–e26
- Miller RJ, Lenihan HS, Muller EB, Tseng N, Hanna SK, Keller AA (2010) Impacts of metal oxide nanoparticles on marine phytoplankton. *Environ Sci Technol* 44(19):7329–7334
- Misra SK, Dybowska A, Berhanu D, Luoma SN, Valsami-Jones E (2012) The complexity of nanoparticle dissolution and its importance in nanotoxicological studies. *Sci Total Environ* 438:225–232
- Montes MO, Hanna SK, Lenihan HS, Keller AA (2012) Uptake, accumulation, and biotransformation of metal oxide nanoparticles by a marine suspension-feeder. *J Hazard Mater* 225–226:139–145
- Mortimer M, Kasemets K, Kahru A (2010) Toxicity of ZnO and CuO nanoparticles to ciliated protozoa *Tetrahymena thermophila*. *Toxicology* 269(2–3):182–189
- Navarro E, Baun A, Behra R, Hartmann NB, Filser J, Miao AJ, Quigg A, Santschi PH, Sigg L (2008) Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. *Ecotoxicology* 17(5):372–386
- Nel A, Xia T, Mädler L, Li N (2006) Toxic potential of materials at the nanolevel. *Science* 311(5761):622–627
- Nowack B, Bucheli TD (2007) Occurrence, behavior and effects of nanoparticles in the environment. *Environ Pollut* 150(1):5–22
- Oberdörster G, Oberdörster E, Oberdörster J (2005) Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ Health Perspect* 113(7):823–839
- Pakrashi S, Dalai S, Sneha Ritika B, Chandrasekaran N, Mukherjee A (2012) A temporal study on fate of Al₂O₃ nanoparticles in a fresh water microcosm at environmentally relevant low concentrations. *Ecotoxicol Environ Saf* 84:70–77
- Pelley AJ, Tufenkji N (2008) Effect of particle size and natural organic matter on the migration of nano- and microscale latex particles in saturated porous media. *J Colloid Interface Sci* 321(1):74–83
- Peralta-Videa JR, Zhao L, Lopez-Moreno ML, de la Rosa G, Hong J, Gardea-Torresdey JL (2011) Nanomaterials and the environment: a review for the biennium 2008–2010. *J Hazard Mater* 186:1–15
- Petosa AdamoR, Jaisi DP, Quevedo IR, Elimelech M, Tufenkji N (2010) Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physico-chemical interactions. *Environ Sci Technol* 44(17):6532–6549
- Petosa AR, Brennan SJ, Rajput F, Tufenkji N (2012) Transport of two metal oxide nanoparticles in saturated granular porous media: role of water chemistry and particle coating. *Water Res* 46(4):1273–1285
- Phenrat T, Saleh N, Sirk K, Tilton RD, Lowry GV (2007) Aggregation and sedimentation of aqueous nanoscale zero-valent iron dispersions. *Environ Sci Technol* 41(1):284–290
- Phenrat T, Saleh N, Sirk K, Kim HJ, Tilton RD, Lowry GV (2008) Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. *J Nanopart Res* 10(5):795–814
- Poland CA, Duffin R, Kinloch I, Maynard A, Wallace WAH, Seaton A, Stone V et al (2008) Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat Nanotechnol* 3(7):423–428
- Porter AE, Gass M, Muller K, Skepper JN, Midgley P, Welland M (2007) Visualizing the uptake of C60 to the cytoplasm and nucleus of human monocyte-derived macrophage cells using energy-filtered transmission electron microscopy and electron tomography. *Environ Sci Technol* 41(8):3012–3017
- Praetorius A, Scheringer M, Hungerbühler K (2012) Development of environmental fate models for engineered nanoparticles—a case study of TiO₂ nanoparticles in the Rhine river. *Environ Sci Technol* 46(12):6705–6713
- Praetorius A, Arvidsson R, Molander S, Scheringer M (2013) Facing complexity through informed simplifications: a research agenda for aquatic exposure assessment of nanoparticles. *Environ Sci Process Impacts* 15(1):161
- Pranisha TS, Kamra AK (1997) Scavenging of aerosol particles by large water drops: 3. Washout coefficients, half-lives, and rainfall depths. *J Geophys Res Atmos* 102(D20):23947–23953

- Quik JTK, Lynch I, Hoecke KV, Miermans CJH, Schamphelaere KACD, Janssen CR, Dawson KA, Stuart MAC, Meent DVD (2010) Effect of natural organic matter on cerium dioxide nanoparticles settling in model fresh water. *Chemosphere* 81(6):711–715
- Quik JTK, Vonk JA, Hansen SF, Baun A, Van De Meent D (2011) How to assess exposure of aquatic organisms to manufactured nanoparticles? *Environ Int* 37(6):1068–1077
- Quik JTK, Velzeboer I, Wouterse M, Koelmans AA, van de Meent D (2013) Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Water Res* 48:269–279
- Quik JTK, Velzeboer I, Wouterse M, Koelmans AA, van de Meent D (2014) Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Water Res* 48:269–279
- Reed RB, Ladner DA, Higgins CP, Westerhoff P, Ranville JF (2012) Solubility of nano-zinc oxide in environmentally and biologically important matrices. *Environ Toxicol Chem* 31(1):93–99
- Reinsch BC, Levard C, Li Z, Ma R, Wise A, Gregory KB, Brown GE, Lowry GV (2012) Sulfidation of silver nanoparticles decreases *Escherichia coli* growth inhibition. *Environ Sci Technol* 46(13):6992–7000
- Rogers NJ, Franklin NM, Apte SC, Batley GE, Angel BM, Lead JR, Baalousha M (2010) Physico-chemical behaviour and algal toxicity of nanoparticulate CeO₂ in freshwater. *Environ Chem* 7(1):50–60
- Rozan TF, Lassman ME, Ridge DP, Luther GW (2000) Evidence for iron, copper and zinc complexation as multinuclear sulphide clusters in oxic rivers. *Nature* 406(6798):879–882
- Saleh NB, Pfefferle LD, Elimelech M (2008a) Aggregation kinetics of multiwalled carbon nanotubes in aquatic systems: measurements and environmental implications. *Environ Sci Technol* 42(21):7963–7969
- Saleh N, Kim HJ, Phenrat T, Matyjaszewski K, Tilton RD, Lowry GV (2008b) Ionic strength and composition affect the mobility of surface-modified Fe₀ nanoparticles in water-saturated sand columns. *Environ Sci Technol* 42(9):3349–3355
- Savić R, Luo L, Eisenberg A, Maysinger D (2003) Micellar nanocontainers distribute to defined cytoplasmic organelles. *Science* 300(5619):615–618
- Schneider T, Jensen KA (2009) Relevance of aerosol dynamics and dustiness for personal exposure to manufactured nanoparticles. *J Nanopart Res* 11(7):1637–1650
- Schrack B, Hydutsky BW, Blough JL, Mallouk TE (2004) Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. *Chem Mater* 16(11):2187–2193
- Seipenbusch M, Binder A, Kasper G (2008) Temporal evolution of nanoparticle aerosols in workplace exposure. *Ann Occup Hyg* 52(8):707–716
- Shoultz-Wilson WA, Reinsch BC, Tsyusko OV, Bertsch PM, Lowry GV, Unrine JM (2011) Role of particle size and soil type in toxicity of silver nanoparticles to earthworms. *Soil Sci Soc Am J* 75(2):365
- Simon-Deckers A, Loo S, Mayne-L'hermite M, Herlin-Boime N, Menguy N, Reynaud C, Gouget B, Carriere M (2009) Size-, composition- and shape-dependent toxicological impact of metal oxide nanoparticles and carbon nanotubes toward bacteria. *Environ Sci Technol* 43(21):8423–8429
- Singh G, Vajpayee P, Khatoon I, Jyoti A, Dhawan A, Gupta KC, Shanker R (2011) Chromium oxide nano-particles induce stress in bacteria: probing cell viability. *J Biomed Nanotechnol* 7(1):166–167
- Sirivithayapakorn S, Keller A (2003a) Transport of colloids in saturated porous media: a pore-scale observation of the size exclusion effect and colloid acceleration. *Water Resour Res* 39(4):1109
- Sirivithayapakorn S, Keller A (2003b) Transport of colloids in unsaturated porous media: a pore-scale observation of processes during the dissolution of air–water interface. *Water Resour Res* 39(12):1346
- Sirk KM, Saleh NB, Phenrat T, Kim H-J, Dufour B, Ok J, Golas PL et al (2009) Effect of adsorbed polyelectrolytes on nanoscale zero valent iron particle attachment to soil surface models. *Environ Sci Technol* 43(10):3803–3808
- Stanier CO, Khlystov AY, Pandis SN (2004) Nucleation events during the Pittsburgh air quality study: description and relation to key meteorological, gas phase, and aerosol parameters special issue of aerosol science and technology on findings from the fine particulate matter supersites program. *Aerosol Sci Technol* 38(sup1):253–264
- Stankus DP, Lohse SE, Hutchison JE, Nason JA (2010) Interactions between natural organic matter and gold nanoparticles stabilized with different organic capping agents. *Environ Sci Technol* 45(8):3238–3244
- Stebounova L, Guio E, Grassian V (2011) Silver nanoparticles in simulated biological media: a study of aggregation, sedimentation, and dissolution. *J Nanopart Res* 13(1):233–244
- Stumm W, Morgan J (1981) *Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters*, 2nd edn. Wiley, New York
- Sunkara B, Zhan J, He J, McPherson GL, Piringer G, John VT (2010) Nanoscale zerovalent iron supported on uniform carbon microspheres for the in situ remediation of chlorinated hydrocarbons. *ACS Appl Mater Interfaces* 2(10):2854–2862
- Suresh AK, Pelletier DA, Wang W, Moon J-W, Gu B, Mortensen NP, Allison DP et al (2010) Silver nanocrystallites: biofabrication using *Shewanella oneidensis*, and an evaluation of their comparative toxicity on Gram-negative and Gram-positive bacteria. *Environ Sci Technol* 44(13):5210–5215
- ter Laak TL, Gebbink WA, Tolls J (2006) Estimation of soil sorption coefficients of veterinary pharmaceuticals from soil properties. *Environ Toxicol Chem SETAC* 25(4):933–941
- Thio BJR, Montes MO, Mahmoud MA, Lee D-W, Zhou D, Keller AA (2012) Mobility of capped silver nanoparticles under environmentally relevant conditions. *Environ Sci Technol* 46(13):6985–6991
- Tian Y, Silvera-Batista C, Ziegler K (2010) Transport of engineered nanoparticles in saturated porous media. *J Nanopart Res* 12(7):2371–2380
- Tian Y, Gao B, Wu L, Muñoz-Carpena R, Huang Q (2012) Effect of solution chemistry on multi-walled carbon nanotube deposition and mobilization in clean porous media. *J Hazard Mater* 231–232:79–87
- Tiede K, Hassellöv M, Breitbarth E, Chaudhry Q, Boxall ABA (2009) Considerations for environmental fate and

- ecotoxicity testing to support environmental risk assessments for engineered nanoparticles. *J Chromatogr A* 1216(3):503–509
- Tiwari AJ, Marr LC (2010) The role of atmospheric transformations in determining environmental impacts of carbonaceous nanoparticles. *J Environ Qual* 39(6):1883
- Tong Z, Bischoff M, Nies L, Applegate B, Turco RF (2007) Impact of fullerene (C60) on a soil microbial community. *Environ Sci Technol* 41(8):2985–2991
- Tosco T, Bosch J, Meckenstock RU, Sethi R (2012) Transport of ferrihydrite nanoparticles in saturated porous media: role of ionic strength and flow rate. *Environ Sci Technol* 46(7):4008–4015
- Tourinho PS, van Gestel CAM, Lofts S, Svendsen C, Soares AMVM, Loureiro S (2012) Metal-based nanoparticles in soil: fate, behavior, and effects on soil invertebrates. *Environ Toxicol Chem* 31(8):1679–1692
- Tovar-Sánchez A, Sánchez-Quiles D, Basterretxea G, Benedé JL, Chisvert A, Salvador A, Moreno-Garrido I, Blasco J (2013) Sunscreen products as emerging pollutants to coastal waters. *PLoS One* 8(6):e65451
- Tsai SJ, Ada E, Isaacs JA, Ellenbecker MJ (2009) Airborne nanoparticle exposures associated with the manual handling of nanoalumina and nanosilver in fume hoods. *J Nanopart Res* 11(1):147–161
- Tufenkji N, Elimelech M (2004) Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ Sci Technol* 38(2):529–536
- Tungittiplakorn W, Lion LW, Cohen C, Kim J-Y (2004) Engineered polymeric nanoparticles for soil remediation. *Environ Sci Technol* 38(5):1605–1610
- Unrine JM, Hunyadi SE, Tsyusko OV, Rao W, Shoultz-Wilson WA, Bertsch PM (2010) Evidence for bioavailability of Au nanoparticles from soil and biodistribution within earthworms (*Eisenia fetida*). *Environ Sci Technol* 44(21):8308–8313
- Velzeboer I, Hendriks AJ, Ragas AMJ, van de Meent D (2008) Aquatic ecotoxicity tests of some nanomaterials. *Environ Toxicol Chem* 27(9):1942–1947
- Verma A, Stellacci F (2010) Effect of surface properties on nanoparticle–cell interactions. *Small* 6(1):12–21
- Wang P, Keller AA (2009) Natural and engineered nano and colloidal transport: role of zeta potential in prediction of particle deposition. *Langmuir* 25(12):6856–6862
- Wang P, Shi Q, Liang H, Steuerman DW, Stucky GD, Keller AA (2008a) Enhanced environmental mobility of carbon nanotubes in the presence of humic acid and their removal from aqueous solution. *Small* 4(12):2166–2170
- Wang Y, Li Y, Pennell KD (2008b) Influence of electrolyte species and concentration on the aggregation and transport of fullerene nanoparticles in quartz sands. *Environ Toxicol Chem* 27(9):1860–1867
- Wang Z, Li J, Zhao J, Xing B (2011) Toxicity and internalization of CuO nanoparticles to prokaryotic alga *Microcystis aeruginosa* as affected by dissolved organic matter. *Environ Sci Technol* 45(14):6032–6040
- Wang C, Bobba AD, Attinti R, Shen C, Lazouskaya V, Wang L-P, Jin Y (2012a) Retention and transport of silica nanoparticles in saturated porous media: effect of concentration and particle size. *Environ Sci Technol* 46(13):7151–7158
- Wang Y, Gao B, Morales VL, Tian Y, Wu L, Gao J, Bai W, Yang L (2012b) Transport of titanium dioxide nanoparticles in saturated porous media under various solution chemistry conditions. *J Nanopart. Res* 14(9):1–9
- Warheit DB, Laurence BR, Reed KL, Roach DH, Reynolds GAM, Webb TR (2004) Comparative pulmonary toxicity assessment of single-wall carbon nanotubes in rats. *Toxicol Sci* 77(1):117–125
- Westerhoff P, Song G, Hristovski K, Kiser MA (2011) Occurrence and removal of titanium at full scale wastewater treatment plants: implications for TiO₂ nanomaterials. *J Environ Monit* 13(5):1195–1203
- Westerhoff P, Kiser A, Hristovski K (2013) Nanomaterial removal and transformation during biological wastewater treatment. *Environ Eng Sci* 30(3):109–117
- Xia T, Kovoichich M, Liang M, Madler L, Gilbert B, Shi H, Yeh JI, Zink JI, Nel AE (2008) Comparison of the mechanism of toxicity of zinc oxide and cerium oxide nanoparticles based on dissolution and oxidative stress properties. *ACS Nano* 2(10):2121–2134
- Adeleye A, Conway J, Perez T, Ruttan P, Keller A Influence of extracellular polymeric substances on the long-term fate, dissolution, and speciation of copper-based nanoparticles (in preparation)
- Yah C, Simate G, Iyuke S (2012) Nanoparticles toxicity and their routes of exposures. *Pak J Pharm Sci* 25(2):477–491
- Yin H, Casey PS, McCall MJ, Fenech M (2010) Effects of surface chemistry on cytotoxicity, genotoxicity, and the generation of reactive oxygen species induced by ZnO nanoparticles. *Langmuir* 26(19):15399–15408
- Yin K, Lo IMC, Dong H, Rao P, Mak MSH (2012) Lab-scale simulation of the fate and transport of nano zero-valent iron in subsurface environments: aggregation, sedimentation, and contaminant desorption. *J Hazard Mater* 227–228:118–125
- Zhang KM, Wexler AS (2004) Evolution of particle number distribution near roadways—part I: analysis of aerosol dynamics and its implications for engine emission measurement. *Atmos Environ* 38(38):6643–6653
- Zhang Z, Kleinstreuer C et al (2005) Comparison of micro- and nano-size particle depositions in a human upper airway model. *J Aerosol Sci* 36(2):211–233
- Zhang Y, Chen Y, Westerhoff P, Hristovski K, Crittenden JC (2008) Stability of commercial metal oxide nanoparticles in water. *Water Res* 42(8–9):2204–2212
- Zhang Y, Chen Y, Westerhoff P, Crittenden J (2009) Impact of natural organic matter and divalent cations on the stability of aqueous nanoparticles. *Water Res* 43(17):4249–4257
- Zhang H, Chen B, Banfield JF (2010) Particle size and pH effects on nanoparticle dissolution. *J Phys Chem C* 114(35):14876–14884
- Zhou D, Keller AA (2010) Role of morphology in the aggregation kinetics of ZnO nanoparticles. *Water Res* 44(9):2948–2956
- Zhou D, Abdel-Fattah AI, Keller AA (2012a) Clay particles destabilize engineered nanoparticles in aqueous environments. *Environ Sci Technol* 46(14):7520–7526
- Zhou D, Bennett SW, Keller AA (2012b) Increased mobility of metal oxide nanoparticles due to photo and thermal induced disagglomeration. *PLoS One* 7(5):e37363
- Zhou D, Ji Z, Jiang X, Dunphy DR, Brinker J, Keller AA (2013) Influence of material properties on TiO₂ nanoparticle agglomeration. *PLoS One* 8(11):e81239

- Zhu X, Cai Z (2012) Behavior and effect of manufactured nanomaterials in the marine environment. *Integr Environ Assess Manag* 8(3):566–567
- Zhu X, Zhu L, Li Y, Duan Z, Chen W, Alvarez PJJ (2007) Developmental toxicity in zebrafish (*Danio rerio*) embryos after exposure to manufactured nanomaterials: buckminsterfullerene aggregates (nC60) and fullerol. *Environ Toxicol Chem* 26(5):976–979
- Zhu X, Zhu L, Chen Y, Tian S (2009) Acute toxicities of six manufactured nanomaterial suspensions to *Daphnia magna*. *J Nanopart Res* 11(1):67–75
- Zhu Z-J, Carboni R, Quercio MJ, Yan B, Miranda OR, Anderton DL, Arcaro KF et al (2010) Surface properties dictate uptake, distribution, excretion, and toxicity of nanoparticles in fish. *Small* 6(20):2261–2265
- Zhu X, Tian S, Cai Z (2012) Toxicity assessment of iron oxide nanoparticles in zebrafish (*Danio rerio*) early life stages. *PLoS One* 7(9):e46286