ENGINEERED NANOPARTICLES AND THE ENVIRONMENT

BIOPHYSICOCHEMICAL PROCESSES AND TOXICITY
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SERIES PREFACE

Scientific progress is based ultimately on unification rather than fragmentation of knowledge. Environmental science is the fusion of physical and life sciences. Physical, chemical, and biological processes in the environment are not independent but rather interactive processes. Therefore, it is essential to address physical, chemical, and biological interfacial interactions in order to understand the composition, complexity, and dynamics of ecosystems. Keeping separate these domains, no matter how fruitful, one cannot hope to deliver on the full promise of modern environmental science.

The Division of Chemistry and the Environment of the International Union of Pure and Applied Chemistry (IUPAC) has approved the creation of an IUPAC-sponsored book series entitled Biophysico-Chemical Processes in Environmental Systems to be published by John Wiley & Sons, Hoboken, NJ. This series addresses the fundamentals of physical-chemical-biological interfacial interactions in the environment and the impacts on: (1) the transformation, transport, and fate of nutrients and pollutants; (2) food chain contamination and food quality and safety; and (3) ecosystem health, including human health. In contrast to classical books that focus largely on separate physical, chemical, and biological processes, this book series is unique in integrating the frontiers of knowledge of both fundamentals and impacts of interfacial interactions of these processes in the global environment.

With the rapid developments in environmental physics, chemistry, and biology, it is becoming much harder, if not impossible, for scientists to follow new progresses outside their immediate area of research by reading the primary research literature. This book series will capture pertinent research topics of significant current interest and will present to the environmental science community a distilled and integrated version of new developments in biophysicochemical processes in environmental systems.

The book Engineered Nanoparticles and the Environment: Biophysicochemical Processes and Toxicity is Volume 4 of this Wiley-IUPAC series. This book comprises 22 chapters by renowned experts on their respective topic and is unique in integrating both fundamentals and impacts of the fate of engineered nanoparticles in the environment pertaining to the source, release, detection, characterization, analysis, exposure, bioavailability, toxicity, risk, transport, transformation, modeling, and application of engineered nanoparticles in soil, water, and organisms. Further, the most modern techniques and research approaches used for sampling, modeling and instrumental analyses of nanoparticles, and various means for the restoration of natural environments contaminated by engineered nanoparticles are discussed.

This book can be used by senior undergraduate and graduate students in environmental sciences and engineering as an advanced reference book on the subject matter to integrate the latest discoveries, development, and future prospects on the research of engineered nanoparticles in the environment and related ecosystems. It is an essential reference for chemists and biologists studying environmental systems, as well as for geochemists, environmental engineers, and soil and water scientists. It will serve as a useful resource book for professors, instructors, research scientists, professional consultants, policy makers, government regulators, and other individuals who are interested in the physicochemical-biological processes and applications of engineered nanomaterials.

Nicola Senesi
Baoshan Xing
Series Editors
Engineered nanoparticles (ENPs, 1–100 nm) are found in an increasing number of consumer products (such as lotions, shampoos, socks, paints, and toys) and applications (e.g., biomedical, electronic, industrial, and environmental) due to the rapid development and implementation of nanotechnology. This technology is one of the most promising new research areas of the twenty-first century and will have dramatic impacts across all scientific fields. Due to their anticipated high-volume production and widespread use, ENPs will be unavoidably introduced into the environment during intentional application, accidental release, and end-of-life-cycle disposal of ENP-enabled products. For example, ENPs have already been reported to enter the environment as a result of ENP-containing paints. Presently, ENP development and application seem to outpace the research on their potential health and environmental risks. Recent toxicological data raises concern over ENP environmental and health impact, which will be largely determined by their fate, distribution, and bioavailability. However, there is also a great deal of potential in discovery, synthesis, and application of nanomaterials to benefit society and the world. Therefore, there is a need for a comprehensive and updated book to systematically collect, integrate, and disseminate the latest information, data, and knowledge on all the aspects related to ENP and the environment (e.g., detection, toxicity, transformation, modeling, application). Therefore, with a systematic and interdisciplinary approach, this book brings together world-renowned international scientists on the subject matter to integrate the latest discoveries, development, and future prospects on the research of ENP in the environment and ecosystems. We envision this book will be useful for the sustainable development of nanotechnology.

There are 22 chapters in this book and these 22 chapters are divided into three parts. Part I has five chapters focusing on the synthesis, application, detection, and characterization of engineered nanoparticles; Part II has nine chapters focusing on the environmental release, fate, distribution, and modeling of engineered nanoparticles; and Part III has eight chapters focusing on the toxicity and risk assessment of engineered nanoparticles under different scenarios. The integrated combination of these 22 chapters provides a comprehensive overview of the characterization, application, environmental processing, modeling, toxicity, and risk assessment of engineered nanoparticles.

This book is a critical and useful reference book for scientists, engineers, professionals, policy makers, and government regulators who are interested in the biophysicochemical processes and applications of engineered nanomaterials. This book is also an important addition to the existing literature on the subject matter. Further, this book can be used by undergraduate and graduate students as well as instructors and professors in environmental, aquatic, soil, agricultural, nano, marine, atmospheric, geological, ecological, biological, and chemical science and engineering. Once more, the book chapter authors are recognized as leading authorities in their field of research and each chapter was rigorously peer reviewed similar to refereed journal articles.

We very much thank all chapter authors and reviewers who graciously volunteered their time and effort, and contributed their knowledge and wisdom to improve the quality and clarity of this book. Volume 4 of the Wiley-IUPAC book series entitled Engineered Nanoparticles and the Environment: Biophysicochemical Processes and Toxicity. We are also highly grateful to the staff of IUPAC and John Wiley & Sons for their strong support and great cooperation in the publication of the book.

Baoshan Xing
Chad D. Vecitis
Nicola Senesi
LIST OF CONTRIBUTORS

A. R. M. Nabiul Afrooz, Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX, USA

Nirupam Aich, Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX, USA

Abdullah N. Al-Dabbous, Department of Civil and Environmental Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, UK; and Crises Decision Support Program, Environment and Life Sciences Research Center, Kuwait Institute for Scientific Research, Kuwait

Karin Aschberger, Joint Research Centre—Directorate F—Health, Consumers and Reference Materials

Anders Baun, Department of Environmental Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

Jeehye Byun, Graduate School of Energy, Environment, Water and Sustainability, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

Zhonghua Cai, Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen, People’s Republic of China

Elizabeth A. Casman, Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA, USA; and Center for Environmental Implications of Nanotechnology, Carnegie Mellon University, Pittsburgh, PA, USA

Frans M. Christensen, Department for Environment, Health and Safety, COWI A/S, Kongens Lyngby, Denmark

Enda J. Cummins, UCD School of Biosystems and Food Engineering, Agriculture and Food Science Centre, University College Dublin, Dublin, Ireland

Denisa Cupi, Department of Environmental Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

Amy L. Dale, Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA, USA; and Center for Environmental Implications of Nanotechnology, Carnegie Mellon University, Pittsburgh, PA, USA

Michael P. DeLorme, DuPont Haskell Global Centers, Newark, DE, USA

Feng Ding, Structure, Dynamics, and Function of Biomolecules Lab, Department of Physics and Astronomy, Clemson University, Clemson, SC, USA

Sukru Gokhan Elci, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

Jorge Garden-Torresdey, Department of Chemistry, University of Texas at El Paso, El Paso, TX, USA

Yuan Ge, State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China; and Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Robert J. Hamers, Department of Chemistry, University of Wisconsin—Madison, Madison, WI, USA

Kimberly N. Heck, Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX, USA
LIST OF CONTRIBUTORS

Patricia A. Holden, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Allison M. Horst, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Keld A. Jensen, Danish Nanosafety Centre, National Research Centre for the Working Environment, Copenhagen, Denmark

Guibin Jiang, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China

Yon Ju-Nam, College of Engineering, Swansea University, Swansea, Wales, UK

Ralf Kaegi, Eawag—Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

Pu Chun Ke, ARC Center of Excellence in Convergent Bio-Nano Science and Technology, Monash University, Parkville, Victoria, Australia

Junyeol Kim, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Thomas R. Kuech, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI, USA

Prashant Kumar, Department of Civil and Environmental Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, UK; and Environmental Flow Research Centre, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, UK

Jamie Lead, Department of Environmental Health Sciences, University of South Carolina, Columbia, SC, USA

Daohui Lin, Department of Environmental Science, Zhejiang University, Hangzhou, People’s Republic of China

Wei Liu, Institute of Chemical Safety, Chinese Academy of Inspection and Quarantine, Beijing, People’s Republic of China

Yanmin Long, Institute of Environment and Health, Jianghan University, Wuhan, People’s Republic of China

Stacey M. Louie, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA, USA; and Center for Environmental Implications of Nanotechnology, Carnegie Mellon University, Pittsburgh, PA, USA

Gregory V. Lowry, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA, USA; and Center for Environmental Implications of Nanotechnology, Carnegie Mellon University, Pittsburgh, PA, USA

Alyssa L. M. Marsico, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

Gangfen Miao, Department of Environmental Science, Zhejiang University, Hangzhou, People’s Republic of China

Arnab Mukherjee, Connecticut Agricultural Experiment Station, New Haven, CT, USA

Niall J. O’Brien, UCD School of Biosystems and Food Engineering, Agriculture and Food Science Centre, University College Dublin, Dublin, Ireland

Bo Pan, Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, People’s Republic of China

Hyunwoong Park, School of Energy Engineering, Kyungpook National University, Daegu, Republic of Korea

Joel A. Pedersen, Departments of Soil Science and Chemistry, and Environments Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI, USA

Jose R. Peralta-Videa, Department of Chemistry, University of Texas at El Paso, El Paso, TX, USA

Jaime Plazas-Tuttle, Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX, USA

Lori A. Pretzer, Department of Chemistry, Rice University, Houston, TX, USA

John H. Priester, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Kirsten Rasmussen, Joint Research Centre—Directorate F—Health, Consumers and Reference Materials

Ken L. Reed, DuPont Haskell Global Centers, Newark, DE, USA

Navid B. Saleh, Department of Civil, Architectural and Environmental Engineering, University of Texas at Austin, Austin, TX, USA

Emppu Salonen, Department of Applied Physics, Aalto University School of Science and Technology, Aalto, Finland

Lars M. Skjolding, Department of Environmental Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

Sara N. Sørensen, Department of Environmental Engineering, Technical University of Denmark, Kongens Lyngby, Denmark
Cheng Sun, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China

Shengyan Tian, College of Marine Science and Engineering, Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin, People’s Republic of China

Richard W. Vachet, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

Chao Wang, College of Marine Science and Engineering, Tianjin Key Laboratory of Marine Resources and Chemistry, Tianjin University of Science and Technology, Tianjin, People’s Republic of China

David B. Warheit, DuPont Haskell Global Centers, Newark, DE, USA

Zoe S. Welch, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA, USA

Jason C. White, Connecticut Agricultural Experiment Station, New Haven, CT, USA

Mark R. Wiesner, Pratt School of Engineering, Duke University, Durham, NC, USA

Michael S. Wong, Department of Chemical and Biomolecular Engineering, Department of Chemistry, Department of Civil and Environmental Engineering, and Department of Materials Science and NanoEngineering, Rice University, Houston, TX, USA

Yao Xiao, Pratt School of Engineering, Duke University, Durham, NC, USA

Baoshan Xing, Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA, USA

Yuqing Xing, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

Bo Yan, Department of Chemistry, University of Massachusetts Amherst, Amherst, MA, USA

Kun Yang, Department of Environmental Science, Zhejiang University, Hangzhou, People’s Republic of China

Cafer T. Yavuz, Graduate School of Energy, Environment, Water and Sustainability (EEWS), Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

Nuoya Yin, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China

Lihong Zhao, Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen, People’s Republic of China

Xingchen Zhao, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China

Jin Zhou, Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen, People’s Republic of China

Qunfang Zhou, State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, People’s Republic of China

Xiaoshan Zhu, Division of Ocean Science and Technology, Graduate School at Shenzhen, Tsinghua University, Shenzhen, People’s Republic of China
PART I

SYNTHESIS, ENVIRONMENTAL APPLICATION, DETECTION, AND CHARACTERIZATION OF ENGINEERED NANOPARTICLES
1

CHALLENGES FACING THE ENVIRONMENTAL NANOTECHNOLOGY RESEARCH ENTERPRISE

STACEY M. LOUIE, AMY L. DALE, ELIZABETH A. CASMAN, AND GREGORY V. LOWRY

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1.1. INTRODUCTION

The emerging field of nanotechnology, defined by the manipulation of matter on the scale of atoms or molecules (1–100 nm), embraces an impressive diversity of public and private initiatives in engineering, materials science, chemistry, and biology. Nanostructured materials with at least one dimension in this nanoscale, and nanoparticles, or particles of matter with two or three dimensions on the nanoscale, and having unique size-dependent properties (ASTM 2006) are of particular interest to risk assessors because of their wide-ranging applications and potential implications for human health and the environment. The field of environmental nanotechnology focuses on research enterprises at the interface between nanotechnology and the environment, including the development of nanomaterials with potential environmental benefits, designing of safe nanomaterials, promotion of sustainable development of those materials (Ai et al. 2011; Yan et al. 2011; Hutchison 2008), and the assessment of those with the potential to cause adverse ecological effects (Wiesner and Bottero 2007).

1.1.1. Environmental Applications of Engineered Nanoparticles

Many nanomaterials exhibit unique or enhanced functionalities relative to their bulk or macroscale counterparts that make them attractive materials for environmental applications. These properties include enhanced reactivity and adsorptivity due to a high specific surface area. Edge effects and lattice strain effects due to high surface curvature may further increase the surface energy of the particles and their reactivity (Auffan et al. 2009). In addition, nanoparticles or thin films with dimensions much smaller than the wavelength of light can exhibit novel optical properties such as surface plasmon resonance or shifts in the optical band gap compared to larger-sized (bulk) materials with the same chemical composition (Link and El-Sayed 1999; Steigerwald and Brus 1990).

Highly anticipated environmental applications of nanotechnology facilitated by the properties of nanoscale materials include improved air and water treatment (Khin et al. 2012; Gaya and Abdullah 2008; Li et al. 2008; Pan and Xing 2008); remediation of contaminated surface waters, groundwater, and soils (Wong et al. 2002); as well as improved detection or monitoring devices (Willets and Van Duyne 2008; Stewart et al. 2008; Kneipp et al. 1999). Potential near-term applications in the energy sector include heat- and wear-resistant coatings for drill bits and gas turbines, coolant additives to improve the efficiency of heat transfer fluids, and more efficient and longer-lived batteries and supercapacitors (Aricò et al. 2005). Nanomaterials are additionally being explored for use in solar cells, hydrogen fuel cells,
thermoelectric materials, carbon capture and sequestration (CCS) technology, and solid-state lighting (HMWVL 2008; Linkov et al. 2009). Other applications of nanomaterials include lightweight, strong carbon nanotube composites to improve the fuel efficiency of airplanes and automobiles, and nanocatalysts to improve the efficiency of a range of industrial processes (Klaine et al. 2012).

1.1.2. Environmental Implications of Engineered Nanoparticles

The antipode of the benefits of nanotechnology is the potential for environmental harm. Toxic effects of carbon-based nanoparticles and metal and metal oxide nanoparticles have been observed in vivo and in vitro in a wide range of organisms (Liu et al. 2013; Schrand et al. 2010). Cellular mechanisms of toxicity may include physical damage, oxidative stress, DNA damage, and interference with protein folding. Inflammation, fibrosis, and allergic responses have been observed in vivo (Hubbs et al. 2011; Nel et al. 2013; Wiesner et al. 2009).

Nanoparticles may have enhanced the ability to penetrate biological barriers and may also distribute differentially in the body according to size (Liu et al. 2013; Schrand et al. 2010). Moreover, the bioavailability and toxicity of nanoparticles released to environmental media at end-of-life depends not only on chemical identity and structure, but also on matrix interactions in consumer products, transformations of nanoparticle during product use, and transformations and interactions in the natural and biological environments encountered after the disposal or release of nanoparticles (Lowry et al. 2012; Nowack et al. 2012).

1.2. CURRENT CHALLENGES IN ENVIRONMENTAL NANOTECHNOLOGY

Challenges facing the environmental nanotechnology research enterprise are briefly discussed in this chapter under four categories: (1) physicochemical transformations of nanomaterials; (2) metrology; (3) toxicity assessment; and (4) exposure modeling for risk assessment. We identify knowledge that is now well established from recent research progress while also discussing new and remaining challenges that will require further research to address.

1.2.1. Physicochemical Transformations of Nanomaterials

Much of the environmental nanotechnology literature has assessed as-produced or pristine (i.e., unmodified by the environment) nanomaterials (Handy 2008; Petosa et al. 2010). Although pristine nanomaterials must still be tested to assess risks encountered early in a material’s life cycle (e.g., human exposures during manufacturing), the recent literature reflects an increasing awareness that nanomaterials will undergo extensive physicochemical transformations in the environment and that transformed species are more relevant to a discussion of environmental risks. Likely transformations include homoaegregation, heteroaggregation, dissolution, chemical reaction, and adsorption of macromolecules. Current research focuses on assessing the extent and rate at which these transformations will occur for various nanomaterials in different environments, quantifying their effects on nanomaterial behavior, and incorporating these processes into risk assessments (Lowry et al. 2012).

1.2.1.1. Aggregation

The fate of nanomaterials (as well as their toxicity, discussed in Section 1.2.3) is determined in large part by the physicochemical changes they undergo in the environment. It is widely accepted that nanoparticles have a propensity to attach to surfaces and that these processes will affect their fate and toxicity. These attachment processes include homoaegregation to form nanoparticle aggregates and heteroaggregation with naturally occurring colloids such as clays, biosolids, or natural organic matter.

Aggregation will influence the rates of nanoparticle gravitational settling and accumulation in sediments and soils. Aggregation studies are often accompanied by classical or “extended” Derjaguin-Landau-Verwey-Overbeek (DLVO) models, which estimate interaction energies to explain trends in attachment behavior. Classical DLVO models account for van der Waals and electrostatic forces; extended DLVO models include additional forces, such as steric and acid–base interactions. Given nanoparticle properties such as the material type, zeta-potential, and properties of the organic coating, DLVO models thus enable qualitative explanations of trends in nanoparticle attachment. For example, the rate of homoaegregation and attachment to like-charged surfaces can be predicted to increase as the pH approaches the isoelectric point of the nanoparticle or as charge screening occurs at high ionic strength for charged metal and metal oxide nanoparticles. Surface oxidation of hydrophobic fullerenes and carbon nanotubes improves their hydrophilicity and hence greatly enhances their dispersibility (Smith et al. 2009). Attachment rates and critical coagulation concentrations may be quantitatively modeled for pristine (i.e., uncoated) nanoparticles using DLVO theory to estimate interaction energies for use in aggregation models.

Although nanoparticle attachment behavior is well predicted for pristine nanoparticles, quantitative predictions of aggregation and deposition behavior from DLVO theory are not yet possible for more realistic or complex systems (Hotze et al. 2010b; Philippe and Schaumann 2014), for example, for nanoparticles coated with macromolecules or in natural matrices presenting heterogeneous surfaces as well as species that may adsorb (such as natural organic matter). Part of this problem lies in the need for more accurate parameters...
adsorption of much smaller particles (e.g., those < 5 nm in diameter) may violate the underlying assumptions of classical DLVO theory, that is, \( k_\alpha \gg 1 \), so new models must be developed to describe their aggregation behavior (Lin and Wiesner 2010). Inhomogeneity in the distribution and density of macromolecular coatings adsorbed to nanoparticles violate assumptions used in typical steric models, so improved models must be developed to account for these effects (Lin and Wiesner 2012).

Empirical models may thus be necessary to predict aggregation behavior. The aggregation behavior of one type of commercial TiO\(_2\) nanoparticles has been successfully described by laboratory experiments in which solution chemistry was systematically varied (Ottofuelling et al. 2011). Applying this approach for other nanomaterials will require a large array of experiments for each nanomaterial of interest. Alternatively, a semi-empirical, multiparameter correlation can be developed to predict aggregation behavior from fundamental particle and adsorbed layer properties and solution chemistry, analogous to a correlation developed for nanoparticle deposition (Phenrat et al. 2010). However, applying this approach requires better characterization methods in order to identify the relevant nanomaterial properties, and additional data are needed to verify whether any single correlation can adequately describe a diversity of nanomaterials. Predictions of homo- and heteroaggregation behavior may ultimately have to be highly empirical in nature, and the uncertainty of the aggregate size distribution and composition will have to be incorporated into risk assessment models, as discussed further in Section 1.2.2.2.

Finally, challenges remain in predicting other consequences of aggregation beyond their attachment behavior, such as changes in biouptake, toxicity, and reactivity (Hotze et al. 2010a).

1.2.1.2. Dissolution and Chemical Transformations

Chemical reactions and dissolution can be key determinants of environmental fate and toxicity. This is particularly true for NPs that are soluble at near neutral pH such as ZnO, Ag, and CuO (e.g., Liu and Hurt 2010; Ma et al. 2012; Reed et al. 2012; Wang et al. 2013). The possibility for dissolution of nanoparticles under natural environmental conditions has important implications for fate because it determines the extent to which nanoparticles will persist and accumulate in a “nano” form versus transform to a dissolved (ionic) form. The known ecotoxicity of many ionic metals (e.g., Cu, Ag, and Zn) prompts additional concerns about the ultimate fate of ions released during nanoparticle dissolution. Knowledge of basic solubility equilibrium models for bulk metals is useful for nanoparticles; for example, more rapid dissolution of metal oxides is observed for nanomaterials at acidic pH, as expected from Pourbaix (Eh–pH) diagrams for the bulk materials. However, size-dependent effects on nanoparticle solubility have been observed (Ma et al. 2012; Meulenkamp 1998).

Chemical transformations may include oxidation or reduction, photoreaction, and, for metal NPs made from soft metals, reaction with naturally occurring ligands such as sulfide and chloride. Reactions can transform the entire nanomaterial, or they may only alter its surface. The interplay of chemical reactions (oxidation, reduction, sulfidation) and physical processes (dissolution, precipitation) has now been well studied for silver nanoparticles (Levard et al. 2012; Liu and Hurt 2010; Liu et al. 2010). For example, sulfidation of the nanosilver surface has been shown to drastically reduce nanoparticle dissolution. The rate and order in which these transformations proceed can even determine the morphology of the transformed nanomaterial, leading alternatively to the formation of a sulfidized shell around an elemental core (as seen in the sulfidation of Ag) or reprecipitation of sulfidized nanoparticles around the original nanoparticle (as seen in the sulfidation of ZnO) (Reinsch et al. 2012; Ma et al. 2013). Photoreactions, which can occur in surface waters and top layers of soils, have been shown to affect the homoaggregation of silver nanoparticles and reduction of ionic silver to form new nanoparticles in the presence of humic substances (Poda et al. 2013; Akaighe et al. 2011). Photooxidation of fullerenes has also been observed, resulting in enhanced fullerene dispersibility.

Transformation rates will determine the ultimate persistence of the nanoscale form in the environment. Nanomaterials with low dissolution rates (e.g., titanium dioxide or sulfidized nanosilver) will persist in their native forms. However, even for nanomaterials with appreciable dissolution rates, continuous inputs of low concentrations can still result in accumulation of significant quantities of the nanomaterial in the environment over long timescales. Identification of key transformations and determination of reaction rates is a major challenge, especially in complex, realistic systems representing a range of redox conditions and a variety of different ligands.

1.2.1.3. Adsorption of Macromolecules

Adsorption of natural macromolecules onto nanomaterials significantly complicates predictions of fate and toxicity behavior of the nanomaterial (Louie et al. 2016; Ottofuelling et al. 2011; Huang et al. 2013a; Yang et al. 2011). The types and concentrations of macromolecules present, the nanomaterial surface properties, and the environmental conditions will determine the composition and physicochemical properties of the adsorbed layer and its subsequent effects on nanomaterial behavior, such as aggregation. Important environmental and
biological macromolecules that are likely to adsorb include natural organic matter and proteins (Louie et al. 2013, 2015; Ghosh et al. 2008). Currently, there is a good qualitative understanding of the effects of adsorbed macromolecules on nanoparticle transport behavior, based on traditional colloid chemistry and polymer adsorption theory (Fleer et al. 1993) and a wealth of recent publications on nanoparticle attachment in the presence of natural organic matter or protein mixtures (e.g., see reviews by Nel et al. 2009; Philippe and Schaumann 2014). Typically, adsorbed macromolecules enhance the stability of nanoparticles against aggregation, by providing steric repulsion or enhanced electrostatic repulsion, although destabilization by charge neutralization or bridging can occur. The effects of coatings on toxicity can be informed by specific mechanisms of uptake and targeting elucidated in drug delivery studies. However, even a qualitative prediction of the effects of coatings on ecotoxicity will require further study since a great variety of processes (e.g., aggregation, photoreaction, further interactions with other environmental macromolecules) can be affected by the presence and type of coating and can affect the overall risk of the nanomaterial.

A quantitative description of the adsorption of environmental macromolecules and their effects on nanoparticle behavior across a variety of nanoparticles under various environmental or biological conditions will be a major challenge. The heterogeneity of naturally occurring macromolecules (e.g., humic substances or proteins) present in each particular environment should be acknowledged: due to competitive adsorption, certain components may adsorb preferentially and influence the particle behavior disproportionately to others. For example, of the thousands of proteins present in human blood plasma, the proteins adsorbed onto nanoparticle surfaces number in the tens and do not necessarily correspond to the most abundant species found in the plasma mixture (Monopoli et al. 2012). For natural organic matter, the presence or removal of small quantities of high molecular weight components significantly affected gold nanoparticle aggregation (Louie et al. 2013, 2015).

Adsorbed coatings can be transformed over time due to exchange, degradation, or desorption of molecules. For example, protein exchange on nanoparticles has been observed (Monopoli et al. 2011), and it is expected that different components from heterogeneous natural organic matter samples will also undergo exchange. Biodegradation of polyethylene glycol covalently bound to a nanoparticle was demonstrated and was accompanied by nanoparticle aggregation due to the loss of the stabilizing polymer arms (Kirschling et al. 2011). As with other physicochemical transformations, the kinetics of these transformations relative to nanomaterial residence time in each compartment (e.g., river, sediment, or organism) require further study in order to determine the most relevant transformed nanomaterials to assess and to incorporate coating transformations into fate or toxicity models.

1.2.2. Nanometrology in Environmental Systems

Large strides have been made within the last decade in the detection and characterization of nanomaterials, particularly in determining the size and speciation of nanomaterials with light scattering, fractionation, and spectroscopic methods. Remaining challenges include nanomaterial detection and characterization in complex environmental media (Alvarez et al. 2009; Klaine et al. 2012; NRC 2013), determination of appropriate standards for characterization (Alvarez et al. 2009; Linkov et al. 2009), and a holistic assessment of existing and future data to identify the key properties and dosimetrics that are needed to predict risk for nanomaterials.

1.2.2.1. Detection

Selective detection methods are required for research studies and will be necessary in order to implement potential environmental regulations on nanomaterials. A summary of methods for characterization of NMs in complex matrices and the advantages and disadvantages of each method is provided in Table 1.1. Total metals detection is now well established for environmental samples using sample digestion methods (e.g., acid or microwave digestion) and measurement techniques such as flame atomic absorption (FAA) or inductively coupled plasma-mass spectroscopy (ICP-MS). However, because the identity of a nanomaterial is partly defined by size, detection of nanomaterials will necessarily require not only a total metal determination but also a method that incorporates particle sizing methods or is sensitive to only nanoscale particles. Therefore, detection can be challenging in complex environmental media when selective detection of nano-sized materials is desired among a mixture of dissolved species, colloids, and bulk solids that may contain a high background concentration of the element of interest.

An initial assessment of an environmental sample for nanomaterials may utilize preparative size fractionation of a sample by ultracentrifugation or ultrafiltration to separate any free nanomaterials from dissolved species and larger colloids; the fractions obtained may then be used in further analyses (e.g., ICP-MS to quantify total metal concentrations). However, interferences such as adsorption of material to the ultrafiltration membrane or heteroaggregation with larger colloids may occur. Analyses that require sample digestion or dissolution will preclude subsequent assessment of nanomaterial size or aggregation state.

Size distributions on either unfractonated or fractionated samples may be obtained using transmission electron microscopy (TEM), dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), and fluorescence correlation spectroscopy (FCS, for fluorescent nanoparticles). TEM and DLS are widely used and provide reliable data for pristine nanoparticles and their homoaggregates. Recently, methods coupling size separation with detection and characterization have shown great promise for nanoparticle characterization in complex media. Size-separation methods...
<table>
<thead>
<tr>
<th>Category</th>
<th>Method</th>
<th>Purpose or Information Obtained</th>
<th>Advantages or Unique Features</th>
<th>Limitations and Possible Biases</th>
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<tbody>
<tr>
<td><strong>Batch separation</strong></td>
<td>Extraction (e.g., solvent, surfactant assisted) or sonication</td>
<td>Sample pretreatment to separate nanomaterials from background matrix components</td>
<td>Aids in further characterization of extracted nanomaterials by reducing matrix interferences</td>
<td>Recovery may be poor and varies by sample matrix Possible modification of nanomaterial properties</td>
</tr>
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<td></td>
<td>Ultrafiltration</td>
<td>Separation of nanomaterials from larger colloids</td>
<td>Ease of application Wide variety of pore sizes available</td>
<td>Possible artifacts due to particle–membrane interactions Possible modification of nanomaterial properties</td>
</tr>
<tr>
<td><strong>Sizing and imaging methods</strong></td>
<td>Dynamic light scattering (DLS)</td>
<td>Size distribution (from diffusion coefficient)</td>
<td>Availability of instrumentation Easy of application</td>
<td>Poor size resolution Models to obtain size distributions from autocorrelation functions may not be accurate Measurements biased toward large aggregates with higher scattering intensity Inability to distinguish size of nanoparticles within heteroaggregates</td>
</tr>
<tr>
<td></td>
<td>Fluorescence correlation spectroscopy (FCS)</td>
<td>Size distribution (from diffusion coefficient)</td>
<td>Selectivity for fluorescent nanoparticles</td>
<td>Poor size resolution Models to obtain size distributions from autocorrelation functions may not be accurate Inability to distinguish size of nanoparticles within heteroaggregates</td>
</tr>
<tr>
<td></td>
<td>Nanoparticle tracking analysis (NTA)</td>
<td>Size distribution (from diffusion coefficient)</td>
<td>Ability to immediately obtain number-averaged size distributions</td>
<td>Smallest particles may not scatter enough light to be observed Inability to distinguish size of nanoparticles within heteroaggregates</td>
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<td></td>
<td>Electron microscopy (transmission electron microscopy (TEM), scanning electron microscopy (SEM))</td>
<td>Imaging; size distribution</td>
<td>Ability to distinguish primary particles within larger aggregates Ability to identify material type by electron diffraction or EDX</td>
<td>Prone to drying artifacts Large number of particles must be counted to obtain size distributions</td>
</tr>
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<td></td>
<td>Chromatographic size separations</td>
<td>Size separation (with detection and characterization using in-line detectors)</td>
<td>High size resolution Separation of free nanomaterials from matrix components</td>
<td>Adsorbed macromolecules may preclude size determination in unknown environmental samples due to effects on density and hence sedimentation rate</td>
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<tr>
<th>Category</th>
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<th>Advantages or Unique Features</th>
<th>Limitations and Possible Biases</th>
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<tbody>
<tr>
<td>Detection and characterization of nanomaterials</td>
<td>Inductively coupled plasma-mass spectrometry (ICP-MS)</td>
<td>Total metal concentrations</td>
<td>High sensitivity</td>
<td>In batch mode, nanoparticles cannot be distinguished from dissolved or colloidal material of same composition</td>
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<td>Single-particle ICP-MS (spICP-MS)</td>
<td>Mass (size) of single particles</td>
<td>High sensitivity</td>
<td>Unable to distinguish homoaggregates of nanoparticles from colloidal particles of equivalent mass in unknown samples (without prior knowledge of primary particle size)</td>
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<td>UV–vis spectroscopy</td>
<td>Identification of nanoscale materials (particularly those with a surface plasmon resonance)</td>
<td>Location and intensity of surface plasmon resonance is sensitive to material size, shape, aggregation state, dielectric environment</td>
<td>Prone to matrix interferences (e.g., high scattering in turbid samples, absorbance of background species)</td>
</tr>
</tbody>
</table>

Flow field flow fractionation (FFF or AF4)  
Size separation (with detection and characterization using in-line detectors)  
High size resolution  
Separation of NMs from matrix components  
Ease of coupling with in-line detectors (e.g., UV–vis absorbance, light scattering, ICP-MS)  
Need for method development to minimize membrane interactions for each sample

Electrospray-differential mobility analysis (ES-DMA)  
Size separation (with detection and characterization using in-line detectors, e.g., condensation particle counter)  
High size resolution  
Modeling of coating thickness in dried state allows estimation of surface coverage of macromolecules  
Not appropriate if hydrated size is needed (e.g., for estimation of steric forces)  
Sample purification may be required for accurate size determination (e.g., to prevent deposition of dissolved species onto the nanoparticles during the electrospray/drying process)
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<tbody>
<tr>
<td>Fluorescence spectroscopy</td>
<td>Identification of nanoscale materials</td>
<td>Ability to characterize and selectively detect fluorescent nanomaterials, for example, carbon nanomaterials (near-infrared fluorescence) and quantum dots</td>
<td>Prone to matrix interferences (e.g., fluorescence quenching)</td>
<td></td>
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<tr>
<td>Hyperspectral imaging (HSI)</td>
<td>Identification of nanoscale materials</td>
<td>Ability to selectively identify nanoparticles in complex environmental and biological matrices</td>
<td>Spectral library must be developed to identify nanomaterials and their interactions with matrix components</td>
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<tr>
<td></td>
<td>Imaging of nanomaterial location in an environment or biological sample</td>
<td>Selective for nanomaterials with strong localized surface plasmon resonance</td>
<td>Spectral library must be developed to identify matrix components interacting with nanomaterials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Imaging of nanomaterial location and associations in biological matrices</td>
<td>Minimal perturbation of biological samples</td>
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<tr>
<td>Surface-enhanced Raman spectroscopy</td>
<td>Characterization of adsorbed organic material</td>
<td>Ability to characterize adsorbed matter directly on the nanomaterial surface</td>
<td>High material quantities may be needed</td>
<td>Purification (e.g., of excess dissolved organic matter) needed for dried samples</td>
</tr>
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<td></td>
<td>Characterization of surface forces; imaging and particle sizing</td>
<td>Ability to assess surface forces at nanometer scale</td>
<td>Artifacts due to AFM tip size</td>
<td>Requirement for sample drying or attachment of nanomaterials to substrate in liquid cell</td>
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<td>Sensitivity to adsorbed macromolecules</td>
<td></td>
<td>Difficult to distinguish nanomaterials present in heteroaggregates</td>
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<tr>
<td>Circular dichroism (CD)</td>
<td>Characterization of conformation and adsorbed mass of macromolecules</td>
<td>Ability to characterize adsorbed matter directly on the nanomaterial surface and in liquid suspension</td>
<td>Applicability limited to optically active, chiral molecules (e.g., proteins)</td>
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<tr>
<td></td>
<td></td>
<td>Possibility to distinguish free and surface-bound species</td>
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<tr>
<td>X-ray photoelectron spectroscopy (XPS)</td>
<td>Characterization of surface species (e.g., speciation of the nanoparticle, functional groups in organic coatings)</td>
<td>Ability to assess speciation and transformations of metal or metal oxide nanomaterials</td>
<td>Detection limit (typically parts per thousand) may preclude identification of all species present</td>
<td>Prone to matrix interferences</td>
</tr>
</tbody>
</table>
include disc centrifugal sedimentation (DCS) and flow field flow fractionation (FFF); detectors incorporated or placed in-line with the separation method include UV–vis absorbance, DLS, static light scattering, ICP-MS, and fluorescence detectors (von der Kammer et al. 2012; Plathe et al. 2013; von der Kammer 2011). Comparisons of these methods have been made for mixtures of pristine nanoparticles or nanoparticles with an organic stabilizer (Dieckmann et al. 2009; Mahl et al. 2011; Domingos et al. 2009; Mitruno et al. 2012).

Environmental samples with high concentrations of background colloids will present challenges to detection and characterization of engineered nanoparticles. Detection in the “native” state of a complex matrix would be desirable but is not always possible. For laboratory samples with known nanomaterial input or nanomaterials synthesized with isotopic ratios that do not naturally exist, analysis of the nanoparticle in a relatively unperturbed natural matrix can be performed using FFF coupled with ICP-MS (Gigault and Hackley 2013). For unknown environmental samples, nanoscale components will be difficult to identify and characterize when attached to other particles in unknown environmental samples. Single-particle ICP-MS methods have shown significant promise for such systems, in which individual nanoparticles are resolved upon sample dilution and can be quantified and characterized by ICP-MS (Montañó et al. 2014; Peters et al. 2015; Mitruno et al. 2012; Tuoriniemi et al. 2012); however, distinguishing aggregates of nanoparticles from larger particles would be difficult without prior knowledge of the primary particle size. Imaging methods (e.g., TEM or SEM-EDX; Tuoriniemi et al. 2014) or detection of nano-specific properties (e.g., a surface plasmon resonance peak in the UV–vis absorbance spectrum) would aid in characterization. Additional sample processing will likely be required prior to the application of most characterization methods (including FFF-ICP-MS; von der Kammer et al. 2011) to determine whether nanoparticles exist in a heteroaggregate and to characterize properties such as size and surface chemistry. Sonication or extraction techniques can be

### TABLE 1.1. (Continued)

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<th>Limitations and Possible Biases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synchrotron methods; x-ray diffraction (XRD)</td>
<td>Speciation of nanomaterials</td>
<td>Ability to assess speciation and transformations of metal or metal oxide nanomaterials</td>
<td>Components present in low percentages may not be identifiable</td>
<td>No spatial information on NMs or locations in sample</td>
</tr>
<tr>
<td>Thermogravimetric analysis</td>
<td>Quantification of organic coatings and detection of carbon-based nanomaterials</td>
<td>Direct determination of adsorbed mass of organic matter on nanoparticles</td>
<td>Separation of nanoparticles from background colloids and dissolved matter required to determine adsorbed mass of organic coatings on nanoparticles</td>
<td>Relatively large (milligram-scale) nanomaterial quantities may be required</td>
</tr>
<tr>
<td>Electrokinetic methods</td>
<td>Characterization of surface charge or potential of hard nanoparticles, and charge/hydrodynamic properties of “soft” macromolecule-coated nanoparticles</td>
<td>Ease of application and availability of instrumentation Possible applications for nanoparticle separation (e.g., using gel or capillary electrophoresis)</td>
<td>Separation of nanoparticles from background colloids required for batch analysis Interpretation of electrophoretic mobility may not be straightforward for coated nanoparticles due to influence of both charge and hydrodynamic properties</td>
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applied (Schierz et al. 2012; Xiao et al. 2011) but may not be very effective at detaching nanomaterials from natural colloids and may result in transformations that interfere with subsequent analyses, alter the original nanomaterial, or lead to undesirable losses due to excessive processing and multiple transfers.

Selective identification and quantification of the engineered nanomaterial of interest will also be difficult, although new techniques have recently been developed. Nanomaterials prepared with fluorescent or isotopic labels can be utilized in laboratory studies (Gigault and Hackley 2013) but will not be found in real environmental samples unless such properties are intrinsic to the nanomaterial (e.g., quantum dot fluorescence). Even then, many environmental constituents can bind to particles or transform them and quench fluorescent signals or may be interfered by background fluorescence. Detection of carbon-based nanomaterials is expected to be challenging due to the high carbon background in environmental samples; however, thermogravimetric analysis (Doudrick et al. 2012; Plata et al. 2012) and near-infrared fluorescence (NIRF) spectroscopy (Schierz et al. 2012) have been demonstrated for selective detection of carbon nanotubes in air, bacteria, and sediment samples. For nanoparticles with unique light scattering spectra (e.g., due to surface plasmon resonance), hyperspectral imaging with enhanced darkfield microscopy can be used for detection and characterization of nanomaterials in complex waters or biological matrices (Badireddy et al. 2012; Mortimer et al. 2014). On the other hand, nanomaterials made from common natural elements such as aluminum and iron (a goal of “green” synthesis for nanomaterials) will be very difficult to identify with ICP-MS or other detection methods due to the large background concentration of these elements in natural samples and the lack of distinguishing characteristics from their bulk counterparts.

1.2.2.2. Physicochemical Characterization Characterization of nanomaterial speciation and surface properties (e.g., surface charge and properties of adsorbed organic layers) is needed to elucidate mechanisms driving nanoparticle behavior and assess transformations. Metal speciation (e.g., metal oxide vs. sulfide) can be determined by high-resolution TEM electron diffraction analysis, SEM with energy-dispersive x-ray (EDX) spectroscopy, or synchrotron methods such as x-ray absorption (XAS) or x-ray fluorescence (XRF) (Kim et al. 2012; Reinsch et al. 2012; Ma et al. 2013; Servin et al. 2012).

Characterization of adsorbed macromolecular layers, which impact aggregation behavior and transport, is particularly challenging. The colloidal behavior of nanomaterials can be highly sensitive to the arrangement and coverage of surface charges and coatings (Borkovec et al. 2012; Huang et al. 2013b). Charge and layer thickness must be measured to assess electrostatic forces, and knowledge of the chemistry of attachment of the molecule to the nanomaterial surface is necessary to determine or predict interactions with naturally occurring macromolecules. Electrophoretic mobility measurements are often reported as apparent zeta-potentials and used to represent surface or adsorbed layer charge; however, these measurements do not accurately represent surface charge or potential for nanoparticles with “soft” or permeable adsorbed coatings that impart drag on the particle and modify charge (Doane et al. 2012). In fact, this feature has been used to model layer thickness and charge from electrophoretic mobility measurements (Phenrat et al. 2010), but model-fitting uncertainties reduced the applicability of this approach (Louie et al. 2012). Small angle neutron scattering has been demonstrated to estimate layer thicknesses of natural organic matter in complex colloidal samples (King and Jarvie 2012). Spectroscopic techniques such as x-ray photon spectroscopy (XPS) (Baer et al. 2010), Fourier transform infrared (FTIR) spectroscopy (Liang et al. 2011), or circular dichroism (CD) (Shao et al. 2011) are useful to assess nanomaterial surface chemistry, functional group attachment, or protein conformations. Most of these adsorbed layer characterization methods will suffer from interferences from background colloids in complex environmental media and will require sample fractionation or pretreatment, which can be a significant challenge due to the possibility for transformation of the nanomaterial.

Determination of the most important characteristics to predict nanomaterial risk is a current challenge. Statistical meta-analyses may help elucidate the most important characteristics, as has been demonstrated for the pulmonary toxicity of carbon nanotubes (Gernand and Casman 2014). However, it has been shown that even relatively simple systems (e.g., nanoparticle deposition to glass beads) could not be explained even when relatively thorough characterization of nanomaterials and coatings was provided (including size, EPM, and adsorbed mass) (Hotze et al. 2014). Studies on the transport behavior of titanium dioxide nanoparticles suggest that homoaggregate formation, size, and morphology may be needed in order to explain straining, blocking, and ripening phenomena observed in deposition studies (Chowdhury et al. 2011; Chan and Vikesland 2014). Toxicity studies with well-controlled variation of basic parameters such as surface charge have shown contrasting trends depending on the nanoparticle core material and toxicity endpoint (e.g., studies by Schaebulin et al. 2011; Lee et al. 2013; Collin et al. 2014), suggesting that a better understanding of the links between several different material properties and toxicity will be required to predict risk. Questions still exist regarding the most appropriate exposure dosimetric (e.g., mass, number, or surface area concentrations) to best describe toxicity (Hull et al. 2012; Teeguarden et al. 2007). In conclusion, additional data and analyses are needed to fully elucidate the most important nanoparticle characteristics needed to explain the exposure and hazard risks of nanomaterials. It may be possible that higher-level parameters can be used to predict risk, analogous to the use of simple...
parameters such as the octanol–water coefficient to estimate bioaccumulation of dissolved contaminants. For example, Westerhoff and Nowack suggest that solid–water partitioning coefficients and attachment efficiency can be used to predict nanoparticle fate and hence exposure risk (Westerhoff and Nowack 2013), and simple nanoparticle evaluation strategies can be designed around these principles. Nel et al. identified oxidative stress as a key predictor for nanomaterial toxicity (Nel et al. 2006); Marquis et al. reviewed additional toxicity assays (Marquis et al. 2009). However, analogous to structure–activity relationships for organic chemicals, further research is also needed to establish the relationship between these predictors and the nanomaterial-specific properties in order to reduce testing requirements for individual materials in specific environmental or biological media.

1.2.3. Nanotoxicology: Experimental Approaches and Modeling

Nanotoxicology is a broad field encompassing research on different nanomaterials, organisms, and ecological systems. We briefly discuss overarching challenges in nanomaterial testing, as well as the challenge of translating results among different types of toxicity studies and incorporating them into a general risk assessment framework.

1.2.3.1. Unique Challenges for Nanomaterial Toxicity Studies

Nanomaterials present unique challenges in toxicity testing that are not encountered for molecular species. Dosing of the nanomaterial can be problematic due to size heterogeneity of the sample or aggregation, which can change not only the exposure concentration (due to settling) (Quik et al. 2011; Hull et al. 2013) but also nanoparticle diffusion through biological coatings, for example, extracellular polymeric substances in biofilms (Wirth et al. 2012; Peulen and Wilkinson 2011) or mucin layers (Wiecinski et al. 2009) as well as uptake by organisms (Zhao and Wang 2012; Hull et al. 2011; Ward and Kach 2009). Subsequent interactions of the nanomaterial with the organism will also differ from that of dissolved organic species, which can partition into the cell interior, or dissolved ionic species that can be taken up via ion transport proteins on the cell membrane. Biouptake of the nanomaterial by organisms may occur via active transport, or the nanomaterial may adsorb onto the outside of cell surfaces (possibly resulting in high local concentrations and/or slow, long-term effects such as delivery of toxic ions from the dissolving nanomaterial). Surface chemistry and the presence of adsorbed coatings will change the interactions or uptake by organisms or cells (Zhu et al. 2013; Nel et al. 2009). These mechanisms of uptake must be better understood to determine the manner in which the organism is exposed and delineate the resulting toxic effects.

Transformations can also occur through interactions with the test organism itself (e.g., adsorption of proteins or biological exudates). The most relevant transformed nanomaterials should be determined and tested in order to realistically assess ecotoxicological risks. For example, sulfidation of silver nanoparticles significantly reduces dissolution and toxicity (Reinsch et al. 2012), and adsorption of natural organic matter can reduce the toxicity of silver or zerovalent iron nanoparticles to bacteria by preventing direct contact with or adhesion onto cells or possibly reacting with reactive oxygen species (ROS) or binding toxic ions (Fabrega et al. 2009; Li et al. 2010). Knowledge of the mode of interaction and the mechanism of toxicity is required to explain or predict the effects of different transformations.

1.2.3.2. Ecotoxicological Approaches

Experimental approaches in the field of nanotoxicology range from high-throughput screening of cell cultures or embryos to large-scale ecotoxicological studies (e.g., trophic transfer studies between organisms or model ecosystem (“mesocosm”-scale) studies that can capture the full complexity of an environmental system). Studies may focus on one or several end points including behavioral changes, genotoxicity, or mortality. Acute testing of high doses of as-produced nanomaterials or chronic testing of low, environmentally relevant doses and forms may be employed. Currently, most toxicity data are the former and may be of little value for predicting impacts from real-world exposures that occur at chronic low doses (NRC 2013). Additional important areas of uncertainty in the nanotoxicology field include chronic and sublethal effects, effects on sensitive subpopulations, ecological effects, transient effects, and potential for biouptake and biomagnification (Klaine et al. 2012).

High-throughput screening of nanomaterials in simple in vitro test systems of cells or embryos allows for rapid screening of nanomaterials and may facilitate the development of structure–activity relationships analogous to those for organic chemicals (Nel et al. 2012, 2013). However, results from in vitro studies may not adequately represent more complex in vivo systems. An additional challenge for the field (not exclusive to nanomaterial toxicity) is the inability of simple in vitro systems to capture the variety of biological interactions and relevant end points, or transformations of the nanomaterial that will ultimately occur in organisms and ecosystems. Therefore, results from high-throughput screening should not be used to draw conclusions about organism- or ecosystem-level effects without substantial supplementary analysis. However, high-throughput screening can be a valid methodology for screening potential toxicity of nanomaterials.

A large number of studies are now available on model test organisms of varying complexity, including Daphnia, clams, earthworms, fish, and plants. Initial studies focused on mortality end points using high doses of nanomaterials, while more recent studies have investigated the effects of low doses of nanomaterials on nonlethal end points such as growth and behavior (Baun et al. 2008). Detailed mechanistic studies, for example, on the effects of nanomaterials on gene expression,
are also being conducted (de Lima et al. 2012). Given the wide array of organisms, exposure media, and test assays (as well as variability in the specific nanoparticle properties in each study), correlation of the effects of nanomaterials on a wide range of sensitive organisms and on ecosystem function remains a challenge.

Mesocosm-scale studies represent a more realistic, albeit more complex, system (Bone et al. 2012; Urine et al. 2012) in which nanomaterials can interact with different abiotic matrices (water column, soils, and sediments) and biota (e.g., bacteria, aquatic animals, and plants). The effects observed in mesocosm-scale systems, combined with thorough assessment of the distribution and fate (e.g., speciation) of the nanomaterial, can then inform the design of complementary laboratory studies on a smaller scale. It can also inform high-throughput screening efforts by determining the relevant form of the nanomaterial to screen and the appropriate target organisms and routes of exposure to test.

Statistical meta-analysis of published data and other approaches to information collection, management, and analysis from the nascent field of nanoinformatics can be useful in the identification of key physicochemical properties and quantification of their importance (Gernand and Casman 2014).

1.2.4. Exposure Modeling for Risk Assessment

Fate models such as those described in Part II are needed to predict the environmental concentrations of nanoparticles released to environmental media and those of their transformation products. Modeling efforts to date have been hampered by an incomplete understanding of the physicochemical transformations discussed earlier (Nowack et al. 2012; Wiesner et al. 2009; Lowry et al. 2012) and practical limitations on data availability. Multimedia models are highly desirable for nanoparticle risk assessment.

1.2.4.1. Unique Challenges for Nanoparticle Fate and Transport Modeling

The necessity for a different paradigm in fate models for nanomaterials compared to well-established frameworks for “conventional” pollutants such as organic molecules and ionic metals is currently a topic of debate (Klaine et al. 2011; Westerhoff and Nowack 2013; Dale et al. 2015). The implementation of regulations for nanomaterials would benefit from the ease of adopting existing mass balance models, and it is possible that such traditional frameworks will be sufficient to accommodate nanomaterials with only minor modifications. However, the debate is ongoing because nanoparticles exhibit some behaviors that are unique to their colloidal nature. Small-scale models, such as those of nanoparticles in soil systems, already benefit greatly from the adaptation of models from colloid science. However, colloid transport models for soils (colloid filtration theory) and aqueous systems (Smoluchowski coagulation theory) are not generally applied to reactive particles, and their successful application at large scales and in complex environments is still a challenge for both nano- and non-nano particulates. Here, we briefly introduce some of the ways in which the particulate nature of nanoparticles may (or may not) affect the choice of modeling framework.

The fate and transport of conventional organic contaminants is often, but not exclusively, described with equilibrium partitioning coefficients, which are typically correlated to the properties or structure of the chemical via linear free energy relationships (LFERs) or quantitative structure–activity relationships (QSARs). This approach allows time-independent predictions of chemical partitioning among different environmental phases and allows bioavailability and exposure to be estimated for any of a wide variety of organic chemicals without requiring extensive experimental studies.

In contrast, equilibrium approximations of partitioning behavior are not considered appropriate for colloids. Instead, the kinetics of aggregation and deposition are described by the attachment efficiency and the collision frequency of the particles and interacting surfaces. However, several questions which remain unanswered by colloid science complicate the application of these heteroaggregation models to nanoparticles, such as the best way to model nonspherical particles and the influence of adsorbed organic coatings (Phenrat et al. 2010). For molecular species, kinetically controlled transformations (e.g., biodegradation and photolysis) can be described as a simple pseudo-first-order mass-based removal. In contrast, rates of nanoparticle transformation are more correctly modeled as a function of surface area or surface properties rather than total particle mass. In fact, reactive nanoscale materials can exhibit unique size-dependent surface properties relative to larger particles that result in a greater-than-proportional increase in reaction rates with a decrease in particle size. Because transformations can also significantly change nanoparticle behavior without completely degrading or modifying the core nanomaterial, models must accommodate transformations in a more complex manner than as a simple removal term. For example, because partial sulfidation of a pristine nanosilver particle dramatically decreases its further sulfidation or oxidation, its reaction kinetics are highly nonlinear and must be described as dependent upon the particle’s previous degree of transformation (e.g., Dale et al. 2013). Steady-state models and those which only allow first-order or second-order linear reaction kinetics cannot accommodate this behavior. Beyond the physicochemical characteristics of the nanomaterial, additional data and models are needed to describe the relationship between aggregation, transformation, and transport processes and the properties of the nanomaterial and the environmental system, such as pH, ionic strength, organic carbon, sulfide, and oxygen. With respect to heteroaggregation, DLVO theory as used in colloid science is not intended to provide accurate quantitative predictions of nanomaterial
aggregation for real environmental systems that have highly complex and variable chemical composition (Hotze et al. 2010b; Philippe and Schaumann 2014), and hence has limited applicability in transport models.

The behavior and toxic effects of neutral organic contaminants are often relatively insensitive to environmental system parameters (e.g., the range of pH or ionic strength found in natural waters). Compounds with acidic or basic moieties and inorganic contaminants, in contrast, are sensitive to environmental conditions, but changes in speciation with pH, ionic strength, and oxidation potential can be described with simple relations (e.g., acidity constants, the Debye–Hückel equation, and the Nernst equation). Regardless of the modeling framework applied, the desirability of empirical relations tying environmental conditions to universal model parameters, such as reaction rates and attachment efficiencies or other descriptors of heteroaggregation, is apparent.

Scaling problems are an additional concern for fate modelers interested in applying colloid models at large scales, since equations that estimate the particle–particle interaction energies between every particle type in a complex system will add exponentially to the already-significant computational burdens and data input demands of a large-scale, multimedia compartment model. Model parameterization is a particular concern. To overcome these hurdles, the most recent approaches to modeling nanoparticle fate in aqueous systems have focused on merging traditional mass balance formulations with semi-empirical physical models of heteroaggregation based on Smoluchowski coagulation theory (Praetorius et al. 2012). Ultimately, the choice of appropriate modeling framework and assumptions will depend on the scale of the model and the questions of interest to the modeler. For example, EPA sediment quality guidelines and water quality criteria for metals are based on the total or acid-soluble concentration rather than an explicit consideration of metal speciation (e.g., the colloidal fraction vs. the particle-bound or truly dissolved ionic fraction). It is not yet clear whether this approach is appropriate for nanoparticles.

1.2.4.2. Data Limitations The desire to promote the economic growth of the nanotechnology industry, ensure the confidentiality of nanoparticle manufacturers’ intellectual property, and protect the privacy of consumers is often at odds with the need for data on nanoparticle manufacturing and use. The lack of publicly available information on nanomaterial production and import volumes and the imperfect understanding of nanoparticle emissions from products preclude the accurate prediction of environmental releases (Wiesner et al. 2009), and limitations on environmental monitoring and detection thwart the measurement of nanoparticle concentrations in the environment (Von der Kammer et al. 2012). Stochastic models report model outputs as statistical distributions and thus better reflect uncertainty in model inputs. However, stochastic approaches are not feasible for complex models with long runtimes. Sensitivity analysis can be applied to determine which model inputs most greatly impact model results and can be used to guide future research efforts.

1.2.4.3. The Need for Multimedia Models The transformations undergone by a nanoparticle during one stage of its life cycle will impact its fate and transport behavior in subsequent stages. Models that capture nanoparticle fate within and between multiple environmental compartments such as soil, water, and sediment, called multimedia models, are therefore needed to describe the complete history of particle transformation. For example, since the majority of nanoparticle mass is removed to the solid phase during sewage treatment and may then be placed on agricultural fields as fertilizers, multimedia models are needed to understand the impact of fertilizer runoff on stream loads of nanoparticles relative to direct discharges of sewage treatment plant effluent. Multimedia models have only recently been developed for nanoparticles, and the field is still in its infancy (e.g., Dale et al. 2015; Liu and Cohen 2014; Meesters et al. 2014). Additionally, a complete understanding of risk will require the development of models that can correctly predict biouptake and trophic transfer. Such models do not currently exist because of insufficient scientific understanding at present with regard to nanoparticle bioavailability and the mechanisms and degree of biouptake for a wide range of organisms.

1.3. CONCLUSIONS

Central challenges facing the nanotechnology research enterprise include the need for a better understanding of the extent and rate of physiochemical transformations of nanomaterials, the need for advances in nanometrology to detect and characterize nanomaterials in complex media, the development of environmentally relevant ecotoxicology assays, and the design of sufficiently detailed fate and transport models.

This volume discusses the current state of knowledge in environmental nanotechnology and presents recent advances in addressing the major challenges facing the research enterprise. Part I of this volume introduces several promising environmental applications of nanotechnology. Parts II and III discuss the environmental implications of nanotechnology. Part II focuses on the fate, transport, and exposure risks of nanomaterials and addresses challenges in exposure modeling and understanding transformations in the environment. Finally, Part III focuses on biotoxicity and hazard risks, from cellular- to ecosystem-scale effects. These chapters provide a broad picture of the scope of the nanotechnology research enterprise and the current and future research directions being pursued.

REFERENCES