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State-of-the-Science Report on Predictive Models and Modeling Approaches for Characterizing and Evaluating Exposure to Nanomaterials

Ecosystems Research Division
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by

John M. Johnston
Ecosystems Research Division
National Exposure Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
960 College Station Rd.
Athens, GA 30605

Michael Lowry, Stephen Beaulieu and Evan Bowles
RTI, International
3040 Cornwallis Road
Research Triangle Park, NC 27709

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Project Officer:
Shannon Sturgeon
Office of Resource Conservation and Recovery
Washington, DC 20024

Work Assignment Manager:
Gerry Laniak
Office of Research and Development
Athens, GA 30605

National Exposure Research Laboratory
Office of Research and Development
Washington, DC 20460

Notice and Disclaimer

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Acronyms

Acronym	Definition
3MRA	Multimedia, Multipathway, Multireceptor Risk Assessment
AAN	average agglomeration number
ADE	advection-dispersion equation
ADME	absorption, distribution, metabolism, and elimination
AGU	American Geophysical Union
AHP	Analytical Hierarchy Process
ALARA	as low as reasonably achievable
ANSI	American National Standards Institute
ARAMS	Army Risk Assessment Modeling System
ASTM	American Society for Testing and Materials
BCF	bioconcentration factor
BIOPLUME	2-D transport model of dissolved hydrocarbons
BSAF	biota sediment accumulation factor
CalTOX	California Total Exposure Model for Hazardous Waste Sites
CBEN	Center for Biological and Environmental Nanotechnology
CEINT	Center for Environmental Implications of NanoTechnology
CFC	critical flocculation concentration
CFT	classic filtration theory
CNT	carbon nanotube
CSC	critical salt concentration
DEFRA	Department for Environment, Food and Rural Affairs
DIAS	Dynamic Information Architecture System
DLVO	Derjaguin and Landau, Verwey and Overbeek
EHP	Environmental Health Perspectives
ENM	Engineered nanomaterials
ENRHES	Engineered Nanoparticles: Review of Health and Environmental Safety
EOR	enhanced oil recovery
EPA	U.S. Environmental Protection Agency
EPI Suite	Estimation Programs Interface Suite
ERED	Environmental Residue Effects Database
ES&T	Environmental Science & Technology
ETH	Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology)
FRAMES	Framework for Risk Analysis in Multimedia Environmental Systems
GIS	geographic information systems
HEAST	Health Effects Assessment Summary Table
HSPF	Hydrological Simulation Program–FORTRAN
HWIR	Hazardous Waste Identification Rule
HYDRUS	water flow and solute transport model in variably saturated porous media
ICON	International Council on Nanotechnology
IOM	Institute of Occupational Medicine
IRIS	Integrated Risk Information System

ISO	International Organization for Standardization
K_d	the equilibrium ratio of the concentration in water to the concentration in the solid
K_h	the equilibrium ratio of the concentration in air to the concentration in water
K_{oc}	organic carbon partition coefficient
MAUT	Multi-Attribute Utility Theory
MAVT	Multi-Attribute Value Theory
MCDA	multi-criteria decision analysis
MEMS	MicroElectroMechanical Systems
MFA	material flow analysis
MIMS	Multimedia Integrated Modeling System
MOA	modes of action
MOC	Method of Characteristics (2-D transport model for groundwater)
MODFLOW	finite difference flow model
MRC	military relevant compounds
MWCNT	multiwalled carbon nanotube
NCEA	National Center for Environmental Assessment
NEMS	NanoElectroMechanical Systems
NIOSH	National Institute for Occupational Safety and Health
NM	nanomaterial
NMT	Nanotechnology, Molecular Nanotechnology
NNI	National Nanotechnology Initiative
NNI	Nanotechnology Now
NP	nanoparticles
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
NSF	National Science Foundation
PAH	polycyclic aromatic hydrocarbon
PEC	predicted environmental concentration
PM	precautionary matrix
PMFA	probabilistic material flow analysis
PNEC	predicted no effect environmental concentration
PRZM	Pesticide Root Zone Model
PZC	point of zero charge
QSAR	quantitative structure-activity relationship
QUAL2K	River and Stream Water Quality Model
RESRAD	Residual Radioactivity Models
SAB	Science Advisory Board
SADA	Spatial Analysis Decision Assistance
SMAA-TRI	stochastic multicriteria acceptability analysis
SMARTEN	Strategic Management and Assessment of Risks and Toxicity of Engineered Nanomaterials
STELLA	modeling software package
TMDL	total maximum daily load
TOPSIS	Techniques for Order Preference by Similarity to Ideal Solution

TOUGH2	general purpose numerical simulation program for porous and fractured media
TRACI	Tools for the Reduction and Assessment of Chemical and Other Environmental Impacts
TRIM	Total Risk Integrated Methodology
UC CEIN	University of California Center for Environmental Implications of Nanotechnology
UCLA	University of California, Los Angeles
UK	United Kingdom
UV	ultraviolet
VoI	value of information
WASP	Water Quality Analysis Simulation Program
WRR	Water Resources Research
WWTP	wastewater treatment plant

Acknowledgements

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Executive Summary

This state-of-the-science review was undertaken to identify fate and transport models and alternative modeling approaches that could be used to predict exposure to engineered nanomaterials (ENMs) released into the environment, specifically, for aquatic systems. The development of modeling frameworks that represent the unique complexities of ENM behavior in the environment is in its infancy, and a critical mass of researchers actively engaged in model development efforts has yet to be achieved. Further, it is widely recognized that there are many obstacles to model development and, in general, to conducting environmental risk assessments of ENMs that provide meaningful information for risk managers. Nevertheless, the U.S. Environmental Protection Agency (EPA) will be required to manage potential risks across the life cycle of ENMs, from production through the disposition of wastewaters and residuals containing ENMs. Therefore, this state-of-the-science review included traditional modeling frameworks as well as approaches that are considered relatively new to environmental modeling science and risk management (e.g., adaptive management, multi-criteria decision analysis). In essence, this review sought to answer five basic questions:

1. What models and approaches have been used successfully to simulate nanomaterial behavior in environmental systems?
2. What models and approaches *cannot* be used to predict exposures to ENMs in ecosystems?
3. What models and approaches can be used in the near term, and what types of predictions can be supported by available models?
4. What techniques can be used to address uncertainties and support risk management decisions in the near term given obvious gaps in information?
5. What does the state-of-the-science suggest with respect to long-term research goals that can be undertaken to improve fate and transport modeling tools for ENMs?

To describe the state-of-the science landscape of fate, transport, and exposure models, we conducted a focused review of the literature (published and grey literature), research centers, conference proceedings, and related organizations (e.g., trade associations). We investigated a wide range of information sources to identify models and methods that could be used in evaluating exposures associated with the environmental release of ENMs. Initially, the information search was limited to current models and approaches used to simulate fate and transport of engineered ENMs in aquatic systems. However, because the literature on environmental exposure modeling of ENMs was extremely limited, the search criteria were expanded to include other types of particles (e.g., aerosols, polymers, and colloids) that exhibit transport behaviors similar to ENMs. In addition, we expanded the scope of our review to include modeling approaches that could be useful to risk managers in the near term (e.g., decision analysis methods). Therefore, the literature review identified (1) specific types of modeling approaches (e.g., colloid models) considered highly relevant to exposure modeling of ENMs, (2) traditional environmental exposure models applied to conventional chemicals, and (3) other approaches that could potentially offer modeling solutions for the exposure assessment of ENMs. In essence, our expanded search recognized that ENMs behave as both chemicals and particles and, because few models have been developed to simulate materials that exhibit properties of both chemicals and particles, we defined the state-of-the-science for exposure modeling in broad terms.

Our review strategy involved the development of a thematic key word search based, in part, on our preliminary review of major reports and literature reviews on the environmental modeling of ENMs. We conducted a systematic search of literature databases using different key word combinations and tailored those searches to focus on the most prolific researchers and specific modeling topics (e.g., excluded health and safety literature). Although we recognized that ENM research is a dynamic field, it quickly became apparent that the majority of cutting-edge research on environmental exposures and modeling of ENMs is attributable to a relatively small subset of scientists and modelers. Specifically, our search strategy included

- Elsevier's on-line technical documents service (ScienceDirect)
- Google Scholar search engine, particularly to identify significant reports
- ISI's on-line technical documents in the Web of Science
- Specific sources on nanotechnology, including nano-specific journals, research centers, and nanotechnology trade association web sites
- Online libraries at the University of North Carolina at Chapel Hill (http://www.lib.unc.edu/) and North Carolina State University (http://www.lib.ncsu.edu/)
- Personal communications with experts in nanotechnology research.

The results of this review are presented in the bibliography in **Section 6**, and a subset of these results in **Appendix A** was organized by topical area (e.g., models currently used in fate and transport simulations of ENMs) to support at-a-glance usage of the information provided in this report.

The review focused on models and approaches that *could* be useful in assessing the multimedia, multipathway impacts associated with nanomaterial releases into the environment; therefore, the evaluation included single media models (e.g., porous media colloid models) that could be integrated into a larger modeling framework, as well as multimedia modeling frameworks and systems. In characterizing the state-of-the-science, we concentrated on fate and transport models for ENMs, i.e., those models designed to predict the migration and transformation of chemicals in the environment in support of exposure and risk assessment. Although we recognized that bioaccumulation may be an important determinant of exposure for certain types of ENMs (e.g., nanoscale metals), the focus of this review was clearly on fate and transport modeling as the means to predict exposure.

The information on fate and transport modeling approaches for ENMs is presented at several levels of detail. For example, we developed summaries of models for specific environmental media (i.e., surface water, subsurface, and biological media) as well as multimedia models. In addition, we present (1) models developed and used specifically to evaluate ENMs, (2) established regulatory models used for risk assessment purposes, (3) models that have *potential* applicability to ENMs, and (4) alternative approaches to traditional environmental fate and transport models. We identified a short list of applicable models and approaches, and developed detailed reviews that could be useful to ENM researchers as a foundation in building a predictive modeling capacity for estimating environmental exposures to ENMs. The detailed reviews also include alternative approaches because risk management decisions are likely to be required before the data and modeling science are sufficiently mature to produce reliable quantitative risk estimates for exposures to ENMs.

Lastly, this report suggests several conclusions regarding the state-of-the-science for environmental fate and transport models and alternative approaches that could be useful in supporting an assessment of the potential environmental exposures to ENMs. These conclusions are intended to inform the development of a long-term research strategy and offer insight into future directions that may be productive. In summary, the conclusions presented in this report are

- Research priorities should continue to emphasize the development of empirical studies to characterize fate and transport behavior under laboratory and field conditions
- Field testing of currently available fate and transport models could provide significant insight into the limitations of these models when applied to ENMs
- Development of new models to replace or modify the partitioning approach used in most multimedia fate and transport models should be a priority given the importance of these concepts for conventional organics
- A parallel research track to adopt alternate approaches describe in this review (e.g., decision analysis) should be pursued to meet immediate needs and provide improved decision-making support as data and models specific to ENMs continue to evolve
- The primary focus of this state-of-the-science review was on ENMs with an organic base and, therefore, a similar review specific to metals should be conducted
- The development of a standard ENM data model that introduces consistency in nomenclature and testing requirements *and* is driven by fate and transport modeling needs would support an integrated approach to data/model development for ENMs.

Chapter 1.0
Introduction

Among the many emerging contaminants confronting the U.S. Environmental Protection Agency (EPA) are the various nanoscale materials used in manufacturing commercial nanotechnology products. Engineered nanomaterials (ENMs)[1] are being incorporated into new commercial products at an increasing rate (Wiesner et al., 2006). There are many unknowns regarding the ecological or human health risk associated with exposure to nanoscale materials used in the manufacturing process or residues released during normal use or after the useful lifetime of the product. Environmental processes such as weathering of ENMs may even create a wide spectrum of additional, ill-defined transformation products. Perhaps the biggest unknown is whether these residues enter (or persist in) the ambient environment in forms or concentrations that pose health or environmental concerns.

To determine the nature and extent of possible exposure to ENMs in the environment, methods will be needed to predict their fate and transport in environmental media, understand the biologically relevant forms of ENMs that persist in the environment and, ultimately, confirm their occurrence in media (e.g., drinking water and foods) to which humans and animals may be exposed. Because of the sheer numbers and variety of ENMs that have been and will be created, and the profound influence of type, purity, purpose, and characteristics (e.g., coated versus uncoated) on the environmental behavior of ENMs, it will be a virtual impossibility to conduct a full battery of tests on each nanomaterial that adequately describes interactions among environmental compartments and biological systems. At the nano scale, chemicals can exhibit behaviors that are unique when compared to behaviors of materials in a larger scale, conventional form[2]. For example, nano-scale materials may exhibit unique electromagnetic and optical properties. In addition, ENMs tend to be more reactive than larger-sized materials due to a much higher surface area to mass ratio, potentially resulting in faster kinetics (e.g., oxidation-reduction reactions, dissolution) than might otherwise be expected.

As suggested in **Figure 1-1**, predictive modeling will be required to represent the relationships among: (1) the manner in which ENMs are released into the environment, (2) the behavior, fate, and transport of ENMs in various environmental compartments, (3) the exposure of human and ecological receptors to ENMs, and (4) the adverse effects to ENMs as exposures occur over time and space. However, these models can only be developed if the foundation of basic information needs for ENMs is met, including chemical-physical properties, environmental behavior, and relevant health and ecological endpoints. Based on the information provided by predictive models, decisions can be supported to invest in additional data collection efforts, consider risk management options, and so forth. As EPA carries out its mission to safeguard public health and

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[1] It is important to distinguish between (1) intentionally produced, *engineered* nanomaterials (ENMs), (2) *naturally occurring* nanomaterials (e.g., soil colloids), and (3) *incidental* nanomaterials produced unintentionally through some anthropogenic process (e.g., combustion by-products). Given the potential need for regulations covering their production, use, and disposal, the focus of this report is on ENMs, though many of the fate and transport concepts and approaches may apply to natural and incidental nanomaterials.

[2] The literature often describes materials sized greater than the nanoscale as bulk materials. Consistent with EPA's National Center for Environmental Assessment (NCEA), we have avoided this use of the term in order to prevent confusion with large-volume, bulk production of materials, which may include the bulk production of ENMs.

the environment from chemical stressors, the information that predictive models provide will be an essential component of the decision-making process regarding safe management, use, and disposal of ENMs.

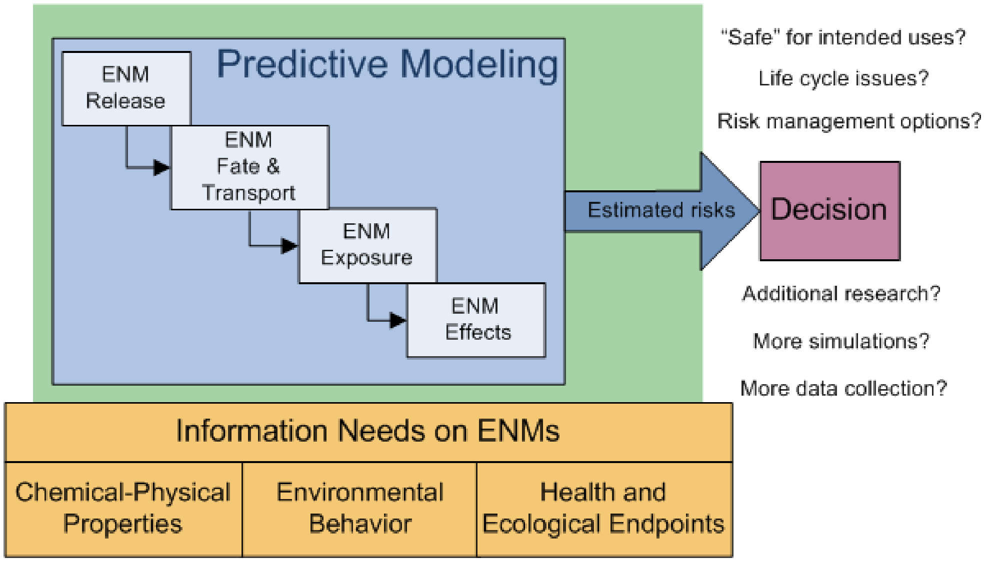

Figure 1-1. A predictive modeling strategy to evaluate ENM risks.

1.1 Background

In considering the information presented in this report, it is first necessary to understand the context for this effort, namely, EPA's conceptual framework for exposure science (US EPA, 2009a). Exposure assessment is the process of measuring and modeling the magnitude, frequency, and duration of contact between the potentially harmful agent and a target population, including the size and characteristics of that population (Zartarian et al., 2005). As shown in **Figure 1-2**, EPA has adapted a source-to-outcome framework to operationalize this definition for the purposes of exposure assessment. Interestingly, this framework includes many of the same features as the predictive modeling strategy illustrated in Figure 1-1. For example, EPA's conceptual framework also begins with the release of a stressor (e.g., ENMs) into the environment and ends with a dose-response characterization to determine the nature and significance of the toxicological endpoints. Following release, ENMs may be transformed and move through environmental media; thus, there is an implicit recognition of the importance of multimedia (versus single medium) behavior. The intensity of the exposure is defined in terms of the concentration in the contact medium, as well as the length of time that a receptor remains in contact with the contaminated medium; the exposure becomes a dose only after the stressor has crossed the body barrier. However, this figure also describes the interactions of environmental factors that contribute to exposure and, importantly, illustrates the types of feedbacks that are possible for ecological receptors and the environment. The impacts of exposure to a chemical stressor in a defined ecosystem or habitat can include a cascade of effects that represent both direct (e.g., significant reduction in a valued species due to direct toxic effects) and indirect (e.g., a shift in the vegetative community) effects. Note that this figure was developed, primarily, to illustrate the importance of these interactions in spatially defined ecosystems in the sense that ecologists often think about the spatial boundaries of an ecosystem (e.g., an old growth forest). The energy and matter fluxes in an ecosystem are tightly coupled to plant and animal communities and, as a result, these feedback loops are common. Although similar types of feedback loops are possible in human exposure scenarios, human-ecosystem feedback is less common for human receptors, because humans tend to be less tightly coupled with their ecosystems.

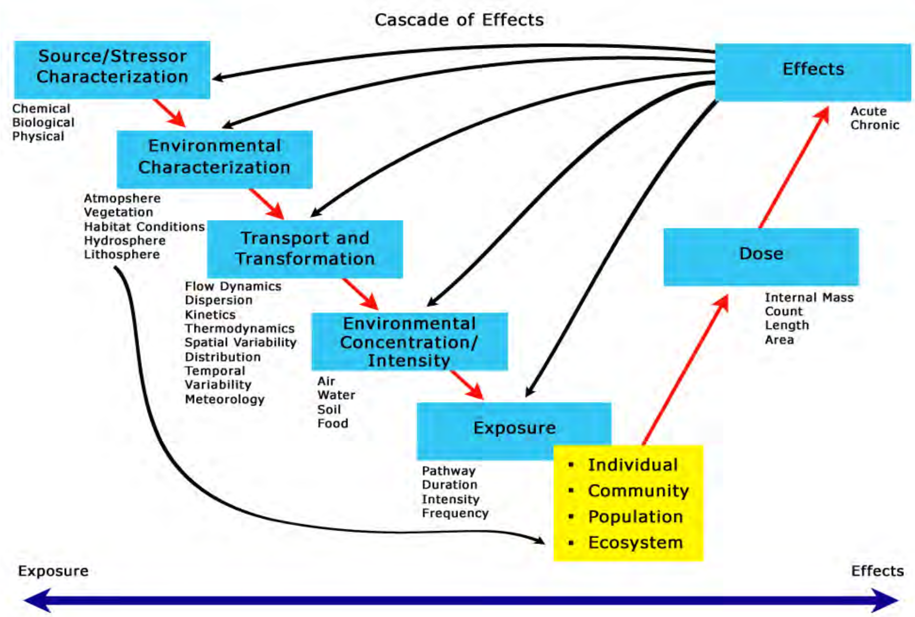

Figure 1-2. Source-to-outcome framework for ecological exposure research (US EPA, 2009a).

Based on this figure, it is clear that exposure science—as evidenced by EPA research programs—seeks to represent the critical processes and flows of materials within an ecosystem as the means of predicting potential effects associated with the introduction of a physical, chemical, or biological stressor. This provides a critical context for this state-of-the-science report, because it suggests that the focus of this review should, appropriately, be on modeling approaches that are capable of representing the complex interactions among ENMs, abiotic, and biotic compartments. Of critical importance is the recognition that nanomaterials are particles and chemicals. This means that traditional partition coefficients (e.g., solid-water partition coefficients) that drive multimedia modeling for most conventional chemicals cannot provide an appropriate theoretical basis with which to predict the environmental exposures to ENMs. In essence, nanomaterials may exist in aqueous solution both in truly dissolved form and as suspended particles; traditional aqueous-solid phase partition coefficients only consider dissolved mass versus mass associated with a stationary solid phase. Furthermore, many processes are of critical importance to ENMs that may not be relevant to the environmental behavior of conventional chemicals (e.g., processes determining the stability of aqueous suspensions of nanoparticles).

Second, it is important to recognize how EPA's research strategy for nanotechnology (US EPA, 2009b) is related to the conceptual framework for exposure science. The purpose of EPA's nanotechnology research program is to conduct focused research to inform risk management decisions under various environmental statutes for which EPA is responsible and, more than likely, under new environmental statutes that will be developed in the future as the nanotechnology industry continues to mature. The EPA research strategy is structured around several research themes and associated science questions. The first research theme is "Sources, Fate, Transport and Exposure" with the associated science questions:

Key Science Question 1. ***What technologies exist, can be modified, or must be developed to detect and quantify manufactured nanomaterials in environmental media and biological samples?***

Key Science Question 2. ***What are the major processes and/or properties that govern the environmental fate, transport, and transformation of manufactured nanomaterials, and how are these related to the physical and chemical properties of those materials?***

Key Science Question 3. ***What are the exposures that will result from releases of manufactured nanomaterials?***

The state-of-the-science report on sampling and analysis (US EPA, 2008) focused on the first key science question, providing a comprehensive review of the literature and research on what is currently available so that the Agency could identify gaps in the technology and methods to detect and quantify ENMs in environmental media. Similarly, this state-of-the-science report focuses on the second and third key science questions through a comprehensive review of the literature and research on currently available models and modeling approaches, so that the Agency can determine what types of research are needed and what the current body of work will and will not support with respect to the prediction of ecological (and human health) exposures to ENMs released into the environment.

Lastly, the National Research Council's (NRC's) publication *Science and Decisions: Advancing Risk Assessment* (NRC, 2009, commonly referred to as the "silver book") provides specific guidance on transport, fate, and exposure assessment that reiterates major themes in both EPA's conceptual framework for exposure science as well as in the Agency's research plan for nanotechnology. Although the silver book primarily focused on human health risk assessment (and, by extension, exposure assessment for human receptors), the insights and recommendations expressed by the Committee clearly resonate with ecological exposure science. For example, among the recommendations that the NRC Committee provided, the following pertain specifically to exposure science:

- Exposure assessment should characterize sources, routes, pathways and the attendant uncertainties linking source to dose
- Recognition of the multiple possible exposure pathways highlights the importance of a multimedia, multipathway exposure framework
- A critical insight that should be recognized by EPA and other practitioners is that there is no ideal transport, fate, or exposure model that can be used under all circumstances

- A lower resolution model (e.g., screening) that produces more timely outputs (at greater uncertainty) may be required to support decisions in the near term when available data and models are not suitable to support a more refined analysis
- Guidelines to help the risk analyst or risk manager understand how model uncertainty and data limitations affect overall uncertainty in exposure assessment are needed
- The communication of uncertainty and variability should be part of key computational steps of risk assessment—e.g., exposure assessment and dose-response assessment.

Several themes emerge from the nexus of these three reports that heavily influenced the development of this state-of-the science report, from the review strategy through the development of criteria with which to evaluate various models and exposure assessment approaches.

- First, multimedia, multipathway exposure frameworks are preferable because they support the development of exposure assessments that reflect the movement of ENMs across and between abiotic and biotic compartments. As suggested in Figure 1-1, the complexities and feedback loops inherent in a functioning ecosystem should be represented to the greatest extent possible.
- Second, currently available models are often not ideal (or in some cases, even useful) for ENMs; the chemical properties required by traditional fate and transport models to simulate major environmental processes (e.g., equilibrium partition coefficients) are not likely to be the same properties that drive those processes for ENMs.
- Third, the purpose of an exposure assessment for ENMs is, ultimately, to support the characterization of potential risks to health and the environment. Consequently, modeling approaches should be considered that will support decisions in the immediate future (i.e., models that could be used right now) as well as approaches that would require additional data and model development. In either case, it will be critical to communicate the uncertainty and variability associated with exposure assessments.

1.2 Purpose and Scope of this Report

The development of modeling frameworks that represent the unique complexities of nanomaterial behavior in the environment is in its infancy, and a critical mass of researchers actively engaged in model development efforts has yet to be achieved. Further, it is widely recognized that there are many obstacles to model development and, in general, to conducting environmental risk assessments of ENMs that provide meaningful information for risk managers (e.g., Greiger et al., 2009, 2010; Wiesner et al., 2009). Nevertheless, EPA will be required to manage potential risks associated with nanomaterials, from the production stage through ultimate discharge and disposal of wastewaters and other residuals containing ENMs. Therefore, this state-of-the-science review included traditional modeling frameworks as well as approaches that are considered relatively new to environmental modeling science and risk management (e.g., adaptive management, multi-criteria decision analysis). Because of the general lack of ENM-specific models, as well as numerous data deficiencies that have been reported in many of the references included in **Section 6**, these alternative approaches may provide a bridge between the immediate management needs for ENMs and the longer term exposure research interests and goals of EPA. We recognize that these alternative approaches cut across risk management and decision analysis sciences; however, given the significant data deficiencies and lack of standardized analytical methods, we believe that it was well within the scope of this report to explore near term solutions to characterizing potential exposures to ENMs. Put succinctly, the purpose of this report on nanomaterial exposure models was to

- Provide a targeted review of the literature (published and grey literature), research centers, researchers, conference proceedings, and entities (e.g., trade associations) that report on current technologies
- Develop a synthesis of promising models and approaches that could be useful in building capabilities in modeling environmental exposures to ENMs, especially for surface water, groundwater, soil, and sediments.

It should be pointed out that this review primarily focused on the fate and transport of ENMs with a base substance composed of an organic chemical (e.g., fullerenes, carbon nanotubes). Given the breadth of this report, we did not specifically investigate the ENMs with a base substance composed of metal (e.g., nano-scale silver). Although many of the concepts and models discussed in this report are relevant to all types of ENMs, the fate and transport modeling of nanoscale metals deserves separate treatment due to the inherent complexities in the environmental behavior of metals (e.g., geochemical speciation, unique sorption-desorption dynamics, nonlinear behavior in the subsurface).

Within the broader context of EPA's mission to protect human health and the environment, the approach taken in this report implies that the domain of models/approaches that were of greatest interest were those that fell into the space identified in **Figure 1-3** by the dashed box.

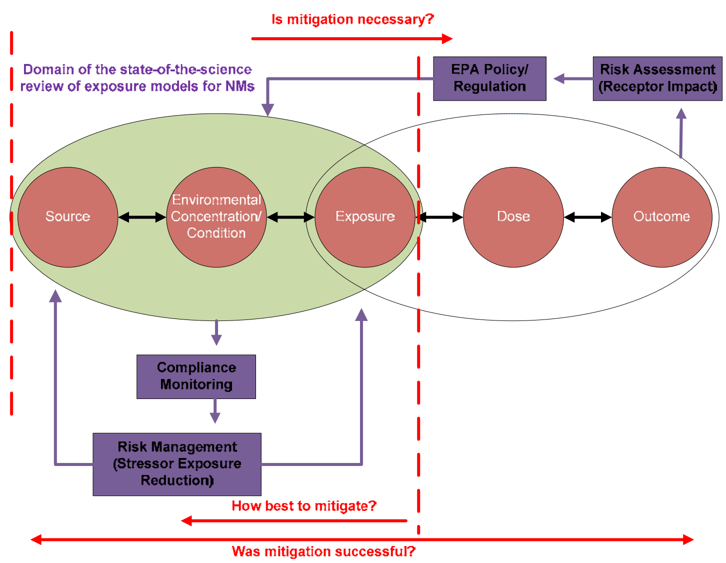

Figure 1-3. Framework for protecting human health and the environment (US EPA, 2009a).

However, some of the alternative approaches that are described in this report are appropriate for the entire framework. Thus, the value of information that could be provided by using, for example, a multi-criteria decision analytic (MCDA) framework or a Bayesian network approach, extends beyond exposure assessment and crosses over into risk management of outcomes.

As in the silver book, we recognized that the universe of potential models was so extensive that we needed to create a set of science questions to guide this review, and focus the state-of-the-science review on exposure models that can be used or adapted for ENMs. Therefore, we developed the following list of questions to guide the review and, ultimately, to organize the conclusions of this review.

1. What models and approaches have been used successfully to simulate nanomaterial behavior in environmental systems?
2. What models and approaches *cannot* be used to predict exposures to ENMs in ecosystems?
3. What models and approaches can be used in the near term, and what types of predictions can be supported by available models?
4. What techniques can be used to address uncertainties and support risk management decisions in the near term given obvious gaps in information?
5. What does the state-of-the-science suggest with respect to long-term research goals that can be undertaken to improve fate and transport modeling tools for ENMs?[3]

This list of questions represents a distillation of the essential goals and purpose of this report and provided a compass that was enormously useful in considering which models to include in this state-of-the-science review.

1.3 Overview of Review Methodology

1.3.1 Information Search and Review

A wide range of information sources was evaluated to identify models and approaches that could be used in evaluating ecosystem exposures associated with the environmental release of engineered ENMs. A literature review was performed to identify specific types of modeling approaches (e.g., colloid models) considered highly relevant to exposure modeling of ENMs, along with other potentially useful modeling frameworks and methods. Sources addressing exposure and environmental fate and transport modeling of ENMs were the primary focus of the search. The search engines ScienceDirect, the ISI Web of Science, and Google Scholar were used extensively to perform the state-of-the-science literature review using different combinations of search criteria described in **Section 3.1**. Titles pertaining to modeling environmental transport of ENMs in soils and aquatic systems were identified and further evaluated, and key sources of information such as key journals, reports, research centers, and informational websites were identified and catalogued. A complete and categorized listing of titles relevant to modeling the fate, transport, and exposure to ENMs released into the environment is presented in **Appendix A**. Each of these references was thoroughly reviewed,

[3] It should be noted that, although this state-of-the-science report is intended to inform the development of long-term research goals, the purpose of this report was *not* to develop long-term research goals.

and a subset of these titles (highlighted in blue) was selected for the detailed model evaluations provided in **Appendix B**.

1.3.2 Characterization of Models and Approaches

The model evaluation framework implemented for this assessment provides a systematic and consistent approach for reviewing and summarizing information about models. The review categories were developed to be consistent with the NRC paper, *Models in Environmental Regulatory Decision Making* (NRC, 2007). In this report, the NRC assesses how models support the EPA's environmental regulatory process. The development and application of regulatory models is described along with recommended considerations for selecting and using models to support EPA programs. The NRC document describes criteria for evaluating whether a model and its results provide a sound basis for regulatory decision making. In reviewing the NRC document, we compiled a series of key considerations for model evaluation and organized them into general categories with specific questions. For example, under the category of *Purpose and Scope*, the types of questions that are relevant include: What is the model purpose?; What transport media are considered?; and What spatial and temporal scales does the model consider?

Because risk management decisions are likely to be required before the data and modeling science are sufficiently matured to reliably produce quantitative risk estimates for ecological exposures to ENMs, we also examined non-traditional modeling frameworks and methods that are more closely related to decision analysis and risk management. These alternative methods do not necessarily fit the traditional mold of environmental fate and transport models but may still be useful in the risk assessment of nanotechnology in the near term.

Figure 1-4 presents a flow chart for characterization of the models identified in the search strategy.

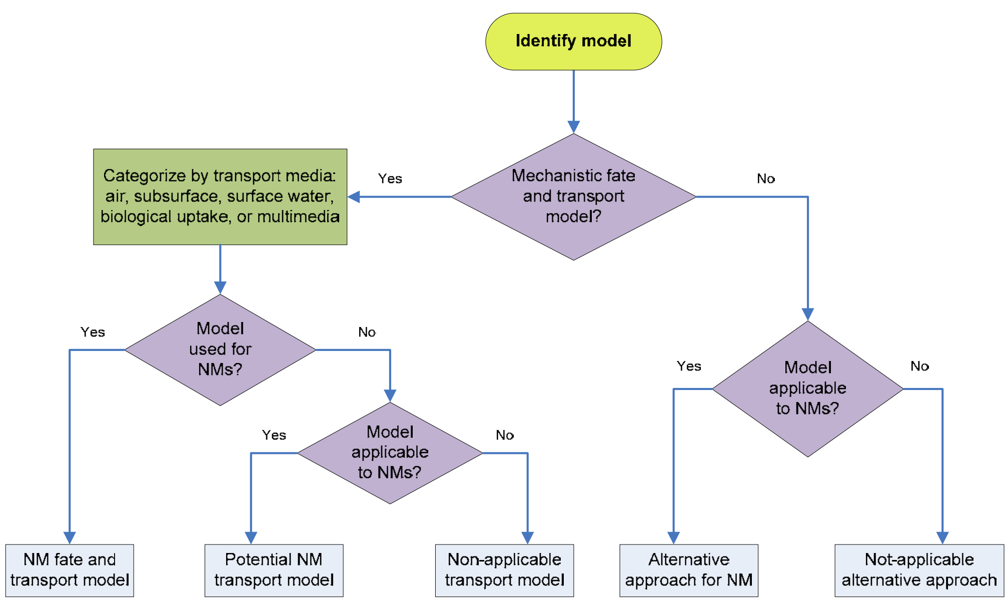

Figure 1-4. Model review process for exposure models and alternative approaches.

1.4 Roadmap to Report

Figure 1-5 presents the organization of this state-of-the-science report. In **Section 2**, we begin by providing a brief overview of how ENMs are defined and classified, describe properties of ENMs that are key determinants of environmental behavior, and identify major processes (e.g., aggregation of particles) that strongly influence the mobility and fate of ENMs in the environment. The purpose of the introductory material in **Section 2** is to provide the reader with general information on ENMs, a refresher of sorts needed to understand the review of exposure models and approaches. Therefore, the presentation of this material was intentionally brief and the reader is encouraged to review any of a number of references included in the bibliography that offer a more thorough treatment of these and other issues, notably, EPA's nanotechnology white paper (US EPA, 2007), EPA's state-of-the-science report on sampling and analysis (US EPA, 2008), *Nanotechnology and the Environment* (Wiesner and Bottero, 2007), *Considerations for environmental fate and ecotoxicity testing to support environmental risk assessment from engineered nanoparticles* (Tiede, et al., 2009), and *Nanomaterials in the environment: behavior, fate, bioavailability, and effects* (Klaine et al., 2008) as excellent sources of information. The remainder of **Section 2** discusses the salient features of exposure modeling for ENMs released into the environment and identifies key challenges associated with predicting exposures to ENMs (e.g., limitations of current risk assessment modeling frameworks).

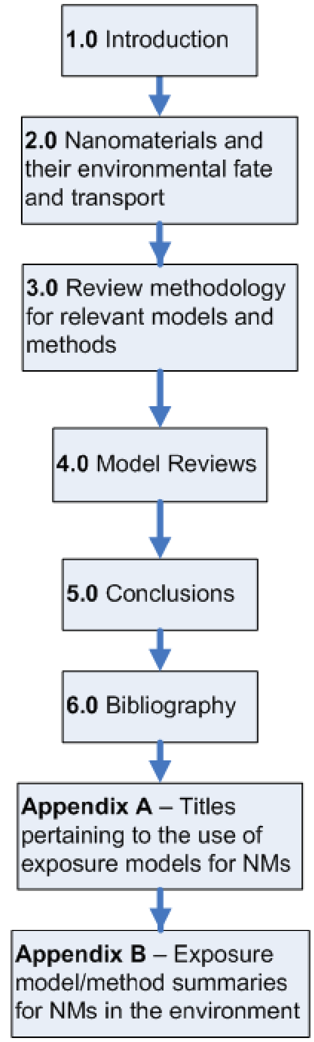

Figure 1-5. Report roadmap.

Section 3 presents the search strategies and key information sources that were included in the search including, for example, major reports, journals, and research centers. **Section 3** then discusses the model/method evaluation criteria that we selected for this state-of-the-science review. Note that the dynamic nature of ENM-related research has resulted in a proliferation of publications over the past several years, with the landscape of relevant literature changing on almost a monthly basis. Therefore, we limited our search to materials that were either published or extracted from other sources (e.g., personal communications) before April 30, 2010. **Section 3** concludes with a summary of major compendia and reviews of models/methods for ENM risk assessment that have been conducted during the past three years. These summary reports were critical in shaping our search strategy and, in addition, we relied on the combination of these reports to ensure that we were not duplicating previous efforts by other researchers. Rather than attempt to identify *every possible* report, article, or paper related to the fate and transport modeling of ENMs, we developed the search/review strategy to describe the state-of-the-science landscape of models and approaches that have been, or could be, useful in developing a research strategy for ENMs. Thus, seminal journal articles, modeling reviews, and major reports were reviewed in detail to ensure that this report captured the state-of-the-science with respect to modeling the fate and transport of ENMs in soil and aquatic systems, and estimating exposures to ecological receptors.

Section 4 summarizes the review methodology and presents results of our review of models and alternative methods used for, or of potential use in, the exposure modeling of ENMs. The descriptions presented in this section distill the information on each model and methodology into practical summaries intended to provide the reader with a thumbnail understanding of the model/method, and its potential relevance to the exposure assessment of ENMs. From this universe of models and methods, we applied the evaluation criteria presented in **Section 4.1** to select the most promising models and approaches and developed the detailed model/method reviews found in **Appendix B**.

Section 5 summarizes our conclusions regarding the state-of-the-science review of models and methods relevant to the exposure assessment of ENMs released into the environment focusing on exposure pathways related to contaminant movement among the soil, subsurface, sediment, surface water, and biological compartments (i.e., this review did not evaluate air models). As discussed above in **Section 1.2**, our purpose was not to solve the problem with this review; rather, the intent was to provide a comprehensive understanding of the types of modeling approaches available and identify those models/methods that could potentially be applied (with or without modification) to predict exposures to ENMs in the environment. Therefore, the conclusions section offers insight into future directions that *may* be productive but does not provide a definitive research agenda for ecological exposure assessment of ENMs.

Section 6 presents a full bibliography of relevant reports, publications, web sites, and communications. This bibliography represents approximately two-thirds of the larger set of references that we identified using our search strategy and initial review. To avoid diluting the references with related but non-essential information, we attempted to focus the bibliography somewhat narrowly on models and methods relevant to ecological exposure modeling. As suggested above in the **Section 3** summary, this bibliography is not comprehensive in the sense that it includes every journal article with any relationship to fate and transport modeling of ENMs. However, this bibliography does represent the state-of-the-science (as published) with regard to fate and transport modeling of ENMs and will provide the reader with a thorough understanding of the models, approaches, gaps, and current research in this field.

Appendix A reorganizes and refines the bibliography to focus on key references, in particular, references for models/methods that are described in more detail in **Appendix B**. The references are organized around five themes

- Exposure science and model evaluation
- Recent reports and compendia
- Models that simulate particle, aerosol, polymer, and colloid behavior
- Multimedia models currently used in ENM fate and transport simulations
- Alternative approaches and models.

Lastly, **Appendix B** presents detailed reviews for exposure models and other relevant alternative approaches (e.g., multi-criteria decision analysis) in a standardized format which includes

- Model Summary
- Key References
- Contact/Availability Information
- Purpose and Scope
- Evaluation (e.g., mathematical representation; complexity; consideration of uncertainty; applicability to ENMs).

Chapter 2.0
Nanomaterials and their Environmental Transport and Fate

This section of the state-of-the-science report provides background information on ENMs and their behavior once released to environmental systems. This background material is needed to understand the review of exposure models and approaches. The presentation of this material is intentionally brief, and the reader is encouraged to review any of a number of references included in the bibliography that offer a more thorough treatment of these issues (US EPA, 2007; Wiesner and Bottero, 2007; Tiede et al., 2009; Klaine et al., 2008).

Section 2.1 defines nanomaterials and describes several nanomaterial classes. Next, **Sections 2.2 and 2.3** discuss the chemical properties and processes that influence the behavior of ENMs in the environment. **Section 2.4** provides a summary of key transport behaviors of ENMs in aquatic and terrestrial environmental systems. This information provides important context for the evaluation of various environmental fate models discussed in **Section 4** (e.g., What properties and processes need to be considered by models of ENM fate and transport?). **Section 2.5** summarizes several major challenges associated with modeling the environmental behavior of ENMs, including transport complexity, variability in types of ENMs, limitations of traditional modeling approaches, and the need for near-term decision making.

2.1 Engineered Nanomaterials and their Classification

ENMs are generally defined as having at least one dimension less than 100 nm and exhibiting properties that are in some way unique relative to the same materials in larger, conventional forms. Some researchers (e.g., Auffan et al., 2009) argue that *only* materials exhibiting novel, scaled behaviors (e.g., surface area-normalized toxicity or adsorption) should be considered from a regulatory perspective differently from conventionally sized materials.

Given the emerging and dynamic nature of nanoscience, consistency in the terminology used to describe NMs in industry and in the academic literature has not yet been achieved, representing a potentially significant source of ambiguity when considering the environmental behavior of ENMs. Several national and international organizations (e.g., ANSI, ASTM) are developing standards for consistent terminology that will, among other things, provide standard definitions of different classes of ENMs. The reader is referred to *ASTM Standard E2456-06, Standard Terminology Relating to Nanotechnology*, for additional information.

Although there are a number of excellent articles and reports describing types ENMs (e.g., US EPA, 2007; Hansen et al., 2007; Ju-Nam and Lead, 2008; Wiesner and Bottero, 2007), we adopted the chemical classification scheme following the work of Klaine et al. (2008), which is based primarily on the chemical composition of the base substance. Importantly, given the broad range of nanomaterial types and properties, this classification system is not internally consistent in all cases. For example, many dendrimers are carbonaceous, and carbon nanotubes and metal oxides can be semiconductors. In addition, important differences exist between ENMs within a given category (e.g., fullerenes versus carbon nanotubes, both of which are carbonaceous ENMs). Additional complications arise from modifications often made to ENMs such as surface coatings that give them desirable properties, altering their basic chemistry and often significantly changing their behaviors with respect to environmental fate and toxicity. Despite these complexities, the classification scheme described below provides a useful overview of the various types of nanomaterials and current applications. Note that the evaluation of fate and transport models in this report focuses mainly on the behavior of organic-based, carbonaceous nanomaterials. Although many of the concepts are relevant to other classes of nanomaterials, important modeling approaches required to evaluate other types of nanomaterials (e.g., geochemical speciation models) were not reviewed in this report.

2.1.1 Carbonaceous ENMs

This class of ENMs is defined by the presence of carbon atoms in the nanomaterial structure. Although carbonaceous ENMs share this fundamental similarity in their chemical composition, there is significant diversity with respect to properties and environmental behavior. For example, fullerenes are 60-carbon-atom hollow spheres also known as buckyballs; carbon nanotubes (CNTs) include multi and single-walled carbon nanotubes. CNTs exhibit strong thermal and electrical conductivity properties. CNTs often have very high aspect ratios, which are similar to the high aspect ratios of asbestos, and thus warrant further toxicity evaluation. Carbon ENMs are often hydrophobic in aqueous systems. Thus, unmodified carbon ENMs typically aggregate together and/or attach to other surfaces in aqueous systems. Significant efforts have been undertaken to reduce their hydrophobicity and to increase the stability of aqueous suspensions (e.g., through functionalization of CNTs with polyethylene glycol or phospholipids). Common applications of carbon ENMs include plastics, catalysts, battery and fuel cell electrodes, super-capacitors, water purification, orthopedic implants, conductive coatings, adhesives and composites, sensors, and as components in electronics, aircraft, aerospace and automotive industries.

2.1.2 Metal ENMs

Metal containing ENMs include metal oxides as well as zero-valent metals. Titanium dioxide has been used as a photocatalyst in solar cells, paints, and coatings. Both titanium and zinc oxide have been used in sunscreens, cosmetics, and bottle coatings due to their UV blocking properties. Cerium dioxide has been applied as a combustion catalyst in diesel fuels, improving emission quality. Cerium dioxide has also been used in solar cells, gas sensors, oxygen pumps, and glass/ceramics.

Nanoparticulate, zero-valent iron has been used extensively for remediation of waters, sediments, and groundwater through chemical oxidation (e.g., of nitrates, chlorinated solvents) (Kanel et al., 2008). It is noteworthy that a voluntary moratorium on the use of zero valent iron nanoparticles for remediation has been in effect in the UK due to unknown potential environmental transport behaviors and impacts.

The use of nanoparticulate silver for its antimicrobial properties represents by far the most prevalent use of ENMs in consumer products (Klaine et al., 2008). Specific applications include medical wound dressings, textiles (e.g., undergarments), air filters, toothpaste, baby products, clothes washing machines and vacuum cleaners. Colloidal gold has also been used in medicine (e.g., tumor therapy) and electronics.

2.1.3 Semiconductor Materials, Including Quantum Dots

Quantum dots are semiconductor nanocrystals. These ENMs have a reactive semiconductor core surrounded by a shell made up of another material (e.g., silica). Quantum dots often include surfactant coatings. The uses have primarily been medical (e.g., imaging) as well as in solar cells and photovoltaics.

2.1.4 Nanopolymers/Dendrimers

This class of ENMs includes polymers with controllable size, topology, and molecular weight. They have many applications in biology, material science, and catalysis. Specific applications include chemical sensors, electrodes, transfecting agents, prion disease therapy, and drug delivery.

2.2 Properties of ENMs that Influence Environmental Behavior

This section provides a summary of key properties that can influence the environmental behavior of ENMs, particularly in aquatic and terrestrial systems. Given their strong surface reactivity and unique behaviors at the nanoscale, different chemical properties can be relevant for ENMs versus conventionally sized chemicals. In addition, nanomaterials exhibit properties of chemicals as well as particles, thus complicating the understanding of their behavior in the environment and requiring a more extensive set of properties when compared to many traditional contaminants. For example, nanomaterials exist in aqueous solution both as truly dissolved molecules as well as suspended particles, so that many traditional partitioning relationships (e.g., K_d [the equilibrium ratio of the concentration in water to the concentration in the solid] relating solid-aqueous phase concentrations) are insufficient to characterize nanomaterial behavior.

Table 2-1 provides a summary listing of the properties discussed in this section and groups the properties into several categories of relevance to ENMs. A primary references for much of the discussion of ENM properties in this section is Chappell (2008).

Table 2-1. Chemical Properties of Nanomaterials Relevant to Environmental Fate and Transport

Size Characteristics	Surface Area and Charge Characteristics	Chemical Composition and Structure Characteristics	Reactivity Characteristics	Partitioning Characteristics
Average particle size	Surface area	Elemental composition	Degradability	Solubility
Particle size range	Specific surface area	Crystalinity	Hydrolysis rate	Effective solubility
Effective particle size	Surface charge	Surface coatings	Biodegradation rate,	Volatility
Aggregate size	Hydrophobicity	Surface functionalization	Photolysis rate	Partition coefficients
Average agglomeration number	Point of zero charge	Aspect ratio	Redox reaction rates	
	Zeta potential	Bulk density		
		Speciation		
		Mean speciation		

2.2.1 Size Characteristics

A sample of ENMs generally contains a distribution of variably sized nanoparticles. Thus, parameters characterizing the size distribution of nanoparticles can be critical. For example, the ***average particle size*** and ***particle size range*** are descriptors often provided by manufacturers. Nanoparticles in aqueous suspensions may be surrounded by more or less permanent layers of molecules due to inter-particle attractive forces. This behavior may result in a far larger ***effective particle size*** relative to the size of the original nanoparticle. Particle aggregates may also be characterized by the ***aggregate size*** and ***average agglomeration number*** (AAN). The AAN is the average number of primary particles contained in an aggregate of particles. The AAN is typically strongly dependent on environmental conditions (e.g., pH, ionic strength) as well as nanoparticle surface coatings. Note that some research communities differentiate between aggregates and agglomerates based on the degree of reversibility of the bonds holding particles together, whereby aggregates are strongly bonded particles and agglomerates are more loosely bound (British Standards Institute, 2007; Luoma, 2008).

2.2.2 Surface Area and Charge Characteristics

The ***surface area*** describes the total exposed surface for a particle. The strong surface activity of ENMs accounts for much of the unique behavior associated with particles in the nano versus larger size range. As the particle size decreases approximately below 20 nm, a very large fraction of the total number of atoms exists at the particle surface, which can give rise to quantum mechanical effects and associated unique properties and behaviors. The related ***specific surface area*** is the ratio of the surface area to the mass for a particle. Some researchers suggest that, due to their surface activity, surface area may be a better measure of potential health effects than concentration, which is mass based (Bell, 2007). For example, some effects may be correlated more closely with the surface area than the concentration (Oberdörster, 1996; Oberdörster et al., 2007; Stoeger et al., 2006, 2007).

The ***surface charge*** is a measure of the density of charged entities on a particle surface and may affect its propensity to interact with other surfaces and ions. The surface charge is typically pH dependent (e.g., with oxide minerals). The surface charge is related to the hydrophobicity and solubility, often determining the stability of nanoparticle suspensions, interactions with other materials (e.g., attachment to natural colloids or immobile soil solids). ***Hydrophobicity*** describes a particles interaction with water. More hydrophobic materials interact to a lesser degree with water molecules, resulting in a reduced affinity for aqueous solutions and greater difficulty in creating stable nanoparticle suspensions. Nanoparticles are often treated in order to decrease their hydrophobicity (e.g., functional groups added to CNTs). The ***point of zero charge*** (PZC) is the pH at which the number of positively charged sites on a surface that interact with protons is equal to the negatively charged sites. This parameter is critical for determining the stability of nanoparticle suspensions and thus their aqueous mobility. Below the PZC, water donates more protons than hydroxide groups, and so the adsorbent surface is positively charged (and attracts anions). Conversely, the surface is negatively charged above PZC (attracting cations/repelling anions). The PZC determines how readily particles will adsorb to surfaces. At the PZC, a colloidal system exhibits ***zeta potential*** of zero (i.e., the particles remain stationary when an electric field is applied). The ***zeta potential*** refers to the electrical potential at a short distance from a particle surface. This potential arises from the surface charge and is often used to approximate the surface potential of the particle.

2.2.3 Chemical Composition and Structure Characteristics

Elemental composition describes what elements make up ENMs. Importantly, the composition of ENMs is often modified with surface coatings or other treatments. A related issue is that the purity of manufactured ENMs varies widely, so that other chemicals are often present within a given batch of ENMs. The ***crystalinity*** refers to the stable three-dimensional arrangement of atoms. The crystalinity can determine or strongly influence other parameters such as surface area, charge, and aspect ratios. In order to maintain stable aqueous suspensions of nanoparticles (without particle aggregation and settling), many ENMs are modified with ***surface coatings*** such as polymers, polyelectrolytes, and surfactants. In addition to the desired changes in the resulting ENM surface chemistry, such modifications may also alter a chemical's environmental transport behavior and toxicity. When surface modifications involve changes in surface functional groups it is referred to as ***surface functionalization***. The ***aspect ratio*** describes the ratio between the longest and shortest lengths of a particle. This parameter can be important for mobility and uptake in organisms.

Speciation refers to chemical form. Different chemical species of the same element often have very different properties influencing environmental fate and toxicity (e.g., solubility, volatility). For some ENMs (e.g., CNTs), surface functionalization can lead to different speciation properties for different parts of the surface, which may be represented by a "mean speciation" of the material's surface (Chappell, 2008). Speciation can strongly influence other properties such as particle size, solubility, and particle charge and, as with all chemicals, speciation can significantly affect the mobility and toxicity of the nanomaterial.

2.2.4 Reactivity Characteristics

The ***degradability*** of ENMs refers to their persistence under various environmental conditions. Generally, only organic ENMs biodegrade, and the rates of biodegradation vary widely. Mineral ENMs typically do not biodegrade; however, they may be differentially susceptible to other degradation/transformation processes such as oxidation.

2.2.5 Partitioning Characteristics

The ***solubility*** refers to whether the material dissolves in water or other substances (e.g., acids, bases, solvents, biological media). In many studies, the dissolved fraction is defined operationally using filters (e.g., dissolved materials are those that pass through a 200 or 450 nm filter). However, the behavior of ENMs below this size fraction can be very different (e.g., aggregation, attachment) than truly dissolved molecules. Therefore, more complete descriptions of nanoparticle suspensions (e.g., particle size distribution, surface activity) and a better understanding of solubility are necessary to fully describe aqueous nanomaterial systems. The ***effective solubility*** reflects the presence of suspended ENM aggregates in addition to truly dissolved molecules. Thus, effective solubilities can vary significantly with environmental conditions (e.g., pH, ionic strength) and can greatly exceed the solubility of conventionally sized materials (Fortner et al., 2005).

2.3 Key Processes Influencing Environmental Behavior

This section describes key environmental processes that influence the mobility and fate of ENMs in aqueous and terrestrial environments. In considering whether a model may be useful for predicting exposures to ENMs, it is critical to understand what processes should be represented within the modeling construct.

2.3.1 Aggregation and Deposition

Both aggregation and deposition of nanoparticles can be considered as a two-step process by which particles are first transported to the proximity of a surface (including for example another particle) followed by an attachment step. In aggregation, particles interact with other moving surfaces while in deposition particles interact with stationary surfaces (including previously deposited particles). As particles are transported and collide in water or air, they may attach to each other through forces of attraction. Particle–particle interactions that control attachment may result from relatively weak van der Waals forces, stronger polar and electrostatic interactions, or covalent bonding (Brar, 2009). The aggregation/disaggregation and attachment/detachment behavior of particulates in aqueous systems may be predicted mechanistically using classic DLVO theory and its extensions (see **Box 2-1**). The term agglomeration is sometimes used interchangeably with aggregation; however, some sources use agglomeration to describe particle groupings that are held together by weaker forces than aggregation. For example, irreversible groupings of primary particles may be referred to as “hard” aggregates in contrast to “soft” (reversible) agglomerates (Brar, 2009).

Box 2-1. DLVO Theory and Its Extensions

Classic DLVO (Derjaguin and Landau, Verwey and Overbeek) theory describes the attractive and repulsive forces between charged surfaces in a liquid medium. The sum of these forces determines whether attraction or repulsion forces will control particle aggregation and attachment behavior. Fundamental DLVO theory accounts for van der Waals attractive forces and electrostatic repulsion (Grasso et al., 2002). Classic DLVO theory has been found inadequate to fully describe particulate behavior in some situations. Additional forces that may be important in environmental systems but are not considered by DLVO theory include hydrogen bonding and the hydrophobic effect, hydration pressure, non-charge transfer Lewis acid base interactions, and steric interactions (Grasso et al., 2002). An additional force active at the nanoscale with potential importance for nanomaterials is Born repulsion (Brant et al., 2007). Other explanations for non DLVO behavior include heterogeneous surface charge conditions (Bradford and Toride, 2007).

Although models of particulate behavior in aqueous systems based on DLVO theory and its extensions may be useful, Brant et al. (2007) emphasize several important issues to consider for potential application of the theory for ENMs. Nanoparticles at the lower size range (approximately smaller than 20 nm) can increasingly resemble molecular solutes, and intermolecular forces can become more important. Particle diffusion (**Section 2.3.5**) can occur at very fast rates for nanoparticles, thereby increasing their potential contact time with other particles and possible attachment surfaces. This contact efficiency may increase the rate of attachment (and decrease mobility) beyond DLVO predictions. Development of extensions to DLVO theory to account for ENM behaviors is an active area of research (e.g., Loux and Savage, 2008).

Because aggregates tend to settle out of solution more readily than primary particles, the aggregation process can have a fundamental influence on the mobility of ENMs. For example, aggregates that settle out will tend to preferentially reside in sediments at the bottom of surface water bodies rather than being entrained within flowing water (if their settling rate is large compared with the hydraulic residence time of the system). In addition, aggregates in porous media may become trapped (filtered) and thus immobile. Aggregates also have a lower surface area to mass ratio than primary particles, so they may be relatively less reactive (Johnson et al., 1996).

The degree of aggregation and deposition is dependent on particle characteristics as well as properties of the environmental system. Important particle characteristics include type, size, and surface properties. Important environmental characteristics include pH, ionic strength, dissolved carbon content, and the presence of dissolved organic matter and multivalent cations. In general, greater aggregation (and settling) occurs under higher ionic strength and pH conditions. A study by Fortner et al. (2005) demonstrated a dependence of C60 suspensions aggregate size distribution on mixing rate, pH, and ionic strength, whereby lower pH and ionic strength led to smaller particles (less aggregation). In many cases, the ionic strength of natural waters is sufficiently large for particles to aggregate and settle to the bottom sediments.

2.3.2 Disaggregation and Detachment

Disaggregation and detachment are essentially the inverse processes relative to aggregation and deposition. Specifically, disaggregation occurs when an aggregate suspended in solution separates in to its component particles. Detachment occurs when a particle detaches from a stationary surface it had previously attached to. In general, processes that favor particle stability (low attachment probabilities) also tend to favor disaggregation and detachment.

2.3.3 Settling and Sedimentation

Settling is the process whereby particulates in aqueous solution sink due to gravity. Settling may lead to sedimentation, the deposition of settled particulates onto sediments present at the bottom of a water body. In very simple systems, the process of settling may be simulated using the Stokes equation, which shows that the settlement velocity is exponentially dependent on the particle diameter. Accordingly, larger particles are much more likely to settle out of suspension. Particles with a settling velocity greater than a critical velocity equal to the mean depth divided by the hydraulic residency time will preferentially be removed from suspension. Particles with a lower settling velocity than the critical velocity will be removed proportionally to the ratio of the settling velocity and the critical settling velocity (Boxall, 2007a). However, in some cases, Stokes law may underpredict the settling velocity of an aggregate by an order of magnitude or more (Wiesner, 1999).

2.3.4 Filtering and Enhanced Transport in Porous Media

Filtering refers to the process whereby aqueous phase particulates are deposited in porous media. Mechanisms for particle filtering include attachment to the porous medium as well as *straining*, which occurs when particulates are too large to pass through pore spaces. The formation of particle aggregates can increase the likelihood of straining and the associated particulate filtering in porous media.

An alternative potential mechanism in porous media is due to *enhanced particle transport* from size exclusion. Because of their size and charge characteristics, particulates may be excluded from some regions of the pore space, flowing primarily within the larger pore spaces. When this occurs, the average velocity of particulates can exceed the average water velocity, thus allowing particulates to travel faster than inert solutes (van de Weerd et al., 1998).

2.3.5 Particle Diffusion

Diffusion refers to the process whereby particles spread from areas of higher concentration to areas of lower concentration. Particle diffusion constants are predicted to be inversely proportional to the particle size, so that the rate of diffusion increases as particle size decreases towards the nanoscale (Brant et al., 2007).

2.3.6 Redox Reactions

Some ENMs are specifically designed to stimulate redox reactions. The redox chemistry often provides the desirable mechanisms responsible for useful applications of ENMs. For example, zero-valent iron has been used extensively in the remediation of waters contaminated with chemicals such as chlorinated solvents. In its nanoscale form, zero-valent iron can undergo the chemical reduction reactions that degrade contaminants faster than larger sized zero-valent iron. Oxidation-reduction reactions can be critical for many ENMs.

2.3.7 Biodegradation

Biodegradation refers to the biologically mediated transformation of chemicals (parent compounds) into other forms (daughter products). Ultimately, the products of biodegradation may be carbon dioxide and water; however, other chemicals may also be formed (in some cases more toxic than the parent compounds). Many ENMs are composed of inherently non-biodegradable inorganic chemicals (e.g., metals) and not expected to biodegrade. However, some carbon ENMs have been shown to be metabolized biologically (Filley et al., 2005). In addition, some polymer based ENMs (and surface coatings) are known to be biodegradable. For some ENMs (e.g., polymers evaluated for use in drug transport), biodegradability is integral to the materials design and function (US EPA, 2007).

2.3.8 Hydrolysis

Hydrolysis describes the reaction of a chemical with water, whereby a chemical bond is broken between a carbon atom and some functional group and a new carbon-oxygen bond is formed with oxygen derived from the water molecule. Hydrolysis generally breaks chemicals down into simpler molecules, which are usually (but not always) less toxic. Given their much greater surface area to mass ratios, ENMs are generally anticipated to undergo transformations such as hydrolysis more readily and at a faster rate than larger-sized materials. However, few ENMs have been thoroughly characterized with respect to hydrolysis, particularly under variable and complex environmental conditions.

2.3.9 Photolysis

Photolysis refers to a reaction whereby a chemical compound is broken down by photons. Photolysis generally breaks chemicals down into simpler molecules, which may be (but are not always) less toxic. Some nanomaterials, such as TiO_2 and C60 are photocatalytic in the sense that when in water and exposed to UV light, they convert energy in photons to chemical compounds that may directly or indirectly react with other compounds in water.

2.3.10 Phase Partitioning

Phase partitioning refers the transfer of mass between aqueous, solid, and air phases, including the processes of dissolution, volatilization, and solid/aqueous partitioning (sorption). Traditionally, equilibrium mass partitioning between solid and aqueous media has been described using partition coefficients (K_d, or the equilibrium ratio of the concentration in water to the concentration in the solid). Equilibrium mass partitioning between water and air has traditionally been characterized using Henry's constants (K_h, or the equilibrium ratio of the concentration in air to the concentration in water). Other partitioning coefficients may characterize the mass uptake into other phases (e.g., plants, fatty tissue). Solubility describes the equilibrium partitioning between a pure solid or liquid phase and water. For non-equilibrium partitioning, mass transfer may be described kinetically using parameters that characterize the rate of mass transfer from one phase to another (e.g., first-order mass transfer rate coefficients).

The field of environmental science has studied the partitioning of various chemicals under a wide range of conditions, yielding extensive summaries of partitioning data used to predict where chemicals will tend to accumulate in the environment (e.g., air, water, soil, fatty tissues). In addition, various approaches for estimating parameters for chemicals based on their chemical structure (e.g., quantitative structure-activity relationships or QSARs) have been developed. This concept of predicting chemical fate based on partitioning behavior is central to most fate/transport and exposure models, and the theoretical underpinnings of phase partitioning (for conventionally sized chemicals) have been widely accepted in risk assessment modeling. However, the utility of existing partition coefficient values and estimation approaches for ENMs is limited given the unique properties and behaviors of chemicals at the nano-scale as discussed below.

ENMs will dissolve to differing degrees into aqueous solution, yielding truly dissolved molecules in addition to nanoscale particulates and larger-sized aggregates suspended in solution. Therefore, nanomaterials in solution exhibit properties and behaviors of chemicals as well as particles. Understanding the dissolution of ENMs is significantly complicated by commonly used operational definitions of solubility (e.g., materials passing through 200 nm filters being considered dissolved; see **Section 2.2.5**). The presence of nanoparticles and associated stable aggregates can greatly increase total concentrations in solution relative to the molecular solubility of a compound. For example, Fortner et al. (2005) show that C60 fullerenes may form negatively charged, water-stable colloidal aggregates, increasing the effective aqueous concentration by approximately 11 orders of magnitude greater than the estimated *molecular solubility* of C60. Given the potentially strong influence of suspended nanoparticulates on the effective aqueous concentrations of ENMs, traditional solubility and partitioning relationships will have limited applicability for predicting the dissolution and the relative mass of ENMs in solid and aqueous phases.

As with aqueous/solid phase mass transfer, the process of chemical volatilization (i.e. aqueous/air phase mass transfer) has traditionally been described using partition coefficients, specifically Henry's constant, which is the ratio of the vapor concentration of a chemical to the aqueous concentration of that chemical. The volatilization of ENMs is also complicated by the potentially significant enhanced solubility effects of nanoparticle suspensions as described above. Therefore, the utility of traditional Henry's constant values may be limited for predicting the partitioning of ENMs to air.

Given their greater surface area per mass ratio and reactivity, it would stand to reason that ENMs could partition at higher rates and thus reach equilibrium more quickly than conventional materials. This behavior may be particularly relevant for mass transfer processes that are kinetically limited (that reach equilibrium relatively slowly). However, this difference in ENM versus conventional chemical behavior has not been extensively evaluated, particularly under variable and complex environmental conditions.

Phase partitioning is also related to biological media and the bioaccumulation of chemicals. Traditional environmental fate evaluations have relied on bioconcentration factors (BCF), which is generally defined as the equilibrium ratio of chemical concentrations in an organism relative to the chemical concentrations in the environmental medium of interest. BCFs characterize the uptake of chemicals to organisms in aqueous environments as well as the uptake of chemicals by plants from soil. Due to the potentially strong influence of ENMs on effective solubility described above, the utility of existing BCFs for the evaluation of the potential to accumulate ENMs in organisms is limited. Furthermore, many researchers have proposed mechanisms of biological uptake that may be possible *only* at the nanoscale (e.g., direct penetration of nanoparticles into organisms).

In summary, because that ENMs exhibit properties of chemicals and particles, partitioning data heavily utilized in traditional environmental fate modeling (e.g., values measured or estimated for K_d and K_h) will not be valid for ENMs. Nevertheless, the ability to predict in which medium substances prefer to exist will still be a critical concept for environmental modeling of ENMs. However, methods of measuring and predicting partitioning for ENMs will need to be modified relative to approaches currently used for chemicals in conventional forms. Specifically, there will need to be (1) new model constructs that accurately capture the complexities of ENM partitioning, and (2) new experimental data will be required to parameterize these models accurately under different environmental conditions.

2.4 Considerations for the Fate and Transport of ENMs in Environmental Media

This section summarizes properties and processes that need to be considered by models of ENM fate and transport. This information provides important context for the evaluation of various environmental fate models discussed in **Section 4**. The discussion first considers behavior in aquatic systems (**Section 2.4.1**) and subsequently considers behavior in terrestrial systems (**Section 2.4.2**). For the purposes of this discussion, aquatic systems are surface waters, whereas terrestrial systems include soils, groundwater, and sediments. **Figure 2-1** provides a summary of fate and transport processes and their relevance to behaviors of ENMs in aqueous versus terrestrial systems. This figure ties together the discussion of processes in **Section 2.3** with the consideration of ENM behaviors in environmental systems, focusing on processes specific to particles like many ENMs versus traditional processes that are often considered in models currently applied for environmental risk assessment.

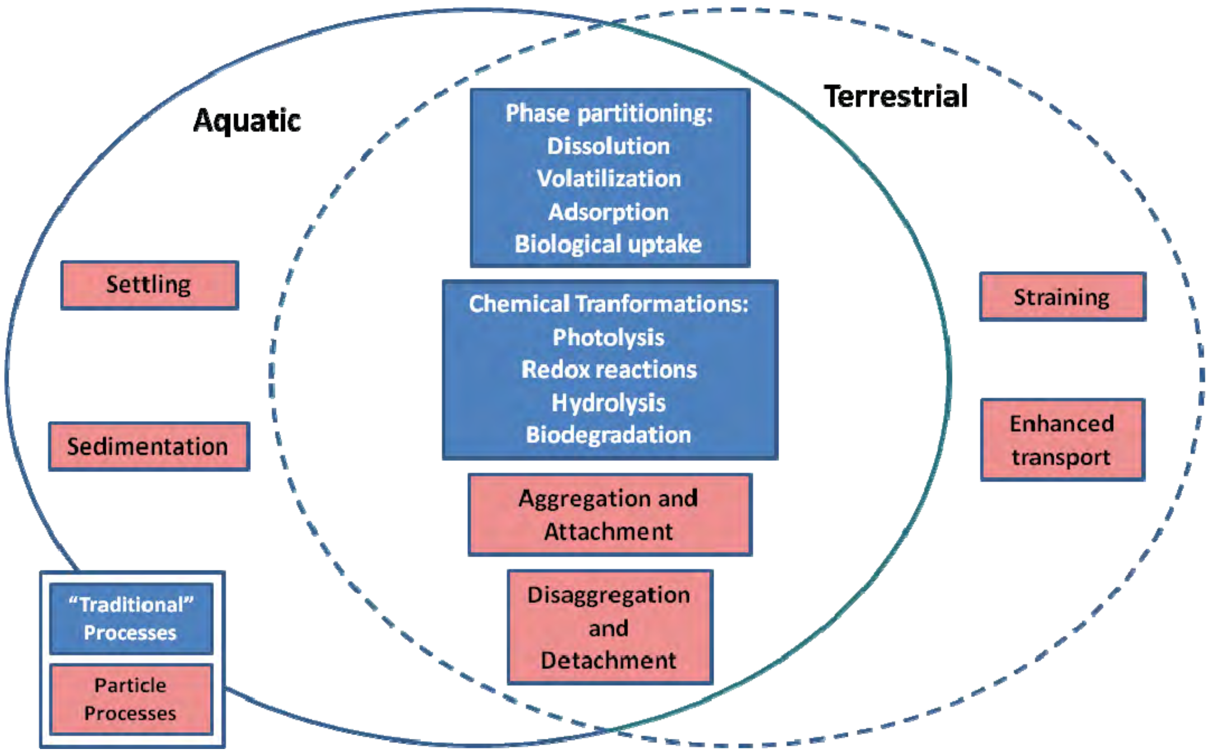

Figure 2-1. Illustration of chemical processes relevant to transport in aquatic (surface water) and terrestrial (groundwater, soils, and sediments) environmental systems.

2.4.1 Fate and Transport in Aquatic Systems

Traditional evaluation of chemical fate in aquatic environmental systems has focused on the following processes and parameters (US EPA, 1996):

- Dissolution characterized by the solubility
- Volatilization characterized by the Henry's constant
- Adsorption to sediments and/or suspended particulates (i.e., solid-aqueous phase partitioning)
- Biological uptake characterized by bioconcentration/bioaccumulation factors
- Photolysis characterized by photolysis rates
- Hydrolysis characterized by hydrolysis rates
- Biodegradation characterized by biodegradation rates.

Many traditional environmental fate assessments consider some or all of the processes listed above. Associated evaluation techniques (e.g., decision frameworks and models) have been developed to predict potential environmental concentrations and to support regulations for a range of environmental contaminants such as pesticides, industrial solvents, and agricultural chemicals. Somewhat less common are environmental fate models that consider processes of aggregation, attachment, settling, and sedimentation. These processes, which involve the behavior of aqueous-phase particulates, are critical in understanding and predicting the environmental fate of ENMs in aqueous systems.

A key consideration influencing the mobility of ENMs in surface waters is whether a distribution of suspended nanoparticles (a nanoparticle suspension) will be stable. In other words, will the nanoparticles tend to aggregate, forming larger assemblies that may settle out, will the nanoparticles tend to hetero-aggregate with other solids in aqueous solution (e.g., soil particles or naturally occurring colloids), or will the nanoparticles remain in a stable suspension? The aggregation/disaggregation process is generally dependent on the solution pH and ionic strength, the presence of other solutes, the properties of naturally occurring particles, and on the properties of the specific ENM (e.g., surface charge, size distribution). Typically, higher pH and ionic-strength solutions give rise to larger particles and subsequent settling. The ionic strength of natural waters (particularly seawater) is often sufficient for particles to aggregate and settle to bottom sediments.

Researchers into ENM behavior in aqueous systems emphasize that surface water chemistry can have a profound influence on the extent of particle aggregation, thus controlling whether nanoparticle suspensions are stable and flow with surface water or are unstable, tending to aggregate and settle (Brar, 2009; Boxall, 2007a). The more prevalent compounds in aquatic ecosystems—proteins, humic acids, organic matter, and natural colloids—may have a profound and complex influence on nanoparticle suspensions and behavior in surface water. Additional research is required to characterize behaviors of ENMs under highly variable natural conditions.

In addition to nanoparticle interactions such as aggregation, ENMs have the capacity to sorb to sediments, other suspended particulates, and/or other solid surfaces (Oberdörster, 2005a). ENMs sorbed to other particulates that are stably suspended in solution (e.g., colloids) would have enhanced mobility relative to nanoparticles that aggregate and settle out of solution.

An additional complexity associated with ENMs in the environment is the impact of transformation processes on ENM properties and behavior. So-called weathering processes occurring in natural systems may include aggregation, hydrolysis, loss or acquisition of surface coatings, photolysis, etc. Each of these processes may have a marked influence on the ENM surface chemistry, reactivity, bioavailability, toxicity, etc. under natural conditions (Brar, 2009). Given their unique properties and behaviors at the nano scale, ENM may be expected to exhibit different transformation behaviors (e.g., rates, dependencies) than conventionally sized materials. The study of ENM transformations is an active field of research (e.g., Hotze et al., 2010).

2.4.2 Fate and Transport in Terrestrial Systems

Traditional evaluation of chemical fate in terrestrial (soil and groundwater) systems has focused on the following processes and parameters (US EPA, 1996)

- Dissolution characterized by the solubility
- Volatilization characterized by the Henry's constant
- Adsorption to organic matter (e.g., organic carbon partition coefficients, K_{oc})
- Adsorption to inorganic matter
- Biological uptake by plants characterized by BCFs
- Photolysis (at the soil surface) characterized by photolysis rate
- Redox reactions and associated rates
- Hydrolysis characterized by hydrolysis rate
- Biodegradation characterized by biodegradation rates.

Many traditional environmental fate assessments consider some or all of the processes listed above. Associated evaluation techniques have been developed to predict potential environmental concentrations and to support regulations for a range of environmental contaminants. Somewhat less common are environmental fate models that consider processes of aggregation, attachment, straining, and enhanced porous media transport. These processes, which involve the behavior of particulates, are critical in understanding and predicting the environmental fate of ENMs in terrestrial systems.

Until the last two decades, subsurface transport was thought to be mediated only by mobile liquid and gaseous phases. However, we now recognize that a separate, solid phase consisting of particles may be present and mobile under some conditions and may facilitate or retard contaminant transport in porous media (Sen and Khilar, 2006). In some cases, contaminants have migrated much farther than would be predicted based on their solubility and sorption characteristics, a behavior that can be explained by colloid-facilitated transport. Such facilitated transport may occur when colloids (and nanoparticles) are excluded from some regions of the pore space due to their size and charge characteristics (e.g., occlusion from zones with small pores and electrostatic repulsion from solid surfaces). Under these conditions, the average velocity of the particulates may exceed the average water velocity (i.e., colloids can travel faster than inert solutes) (van de Weerd et al., 1998). In contrast to the enhanced mobility associated with colloid facilitated transport, colloid transport has also been associated under some conditions with reduced contaminant transport through porous media (Sen, Mahajan, et al., 2002; Sen, Nalwaya, et al., 2002; Bekhit and Hassan, 2005). Retardation of transport may occur when colloidal particles are filtered (trapped) within a porous medium due to their size and/or due to attachment to immobile solid surfaces. Filtering of particulates will be enhanced under conditions favoring aggregation and attachment. A related transport retardation mechanism may occur when particulates plug the pore space and thereby reduce the hydraulic conductivity and groundwater flow velocities.

Colloidal particles may be contaminants (e.g., radioactive metal particulates, nanoparticles with potentially toxic properties) or the particles may mediate the transport of other contaminants in the subsurface (e.g., chemicals or nanoparticles sorbed to and thus potentially migrating with the colloidal particles). With their high surface area to volume ratios, the surface activity of colloids may be very high, potentially leading to faster kinetics and irreversible association (e.g., fast, irreversible sorption).

Colloids generally may undergo the following relevant behaviors in the subsurface:

- Attachment (also called colloid deposition) generally refers to the binding of colloidal particles onto the stationary soil solid surface
- Detachment (also called colloid release) generally refers to the release of colloids from the soil surface into the flowing liquid phase
- Aggregation refers to the process whereby colloids join together forming larger sized aggregates; in many cases these particles may be too large to fit through aquifer pore spaces, and are filtered by the porous medium and no longer migrate with the flowing groundwater (they may also clog a porous medium, reducing its hydraulic conductivity)
- Disaggregation refers to the breaking apart of colloid aggregates (the opposite of aggregation).

There is typically an abundance of natural colloidal particles attached to soil grain surfaces in the environment (e.g., clay colloids, humic and fulvic acids). Under certain conditions, these colloids can be released from the soil matrix and transported with the mobile liquid phase. Mechanisms leading to colloid mobility could include an increase in the groundwater flow rate (e.g., around a pumping well), which may result in sufficient advective shear forces for colloid detachment. An additional important detachment mechanism is tied to the aqueous geochemistry. For example, a decrease in the salt concentration below the *critical salt concentration* (CSC) may release colloids from the solid by decreasing the attractive forces and increasing the repulsive forces between the colloids and the soil (Blume et al., 2005). Note that this behavior is analogous to the *critical flocculation concentration* (CFC) in surface waters, which refers to the concentration above which flocculation is favored (e.g., flocculation in wastewater treatment settlement reactors). These properties are also related to the zeta potential and the point of zero charge as described in **Section 2.2.2**. Groundwater generally has higher ionic strength than rainfall but lower ionic strength than marine and many freshwater systems. Typically, higher ionic strengths increase the likelihood of particle aggregation and attachment due to the reduced inter-particle electrostatic repulsion.

The primary relevant processes determining colloid transport behavior include advection, dispersion, particle-particle physico-chemical interactions, and particle-soil physico-chemical interactions. Other potentially relevant phenomena include acid-base relationships, steric repulsions (e.g., with long-chain polymers), and magnetic interactions (e.g., with iron) (Tosco and Sethi, 2009).

As described in **Section 2.3**, nanoparticle surface modifications and coatings can greatly influence their transport behavior. One application of such surface coatings is for zero-valent iron nanoparticles utilized in the remediation of groundwater contamination (e.g., chlorinated solvents). If the iron nanoparticles are made more hydrophilic through surface modifications, nanoparticle aggregation is greatly reduced along with potential sorption and filtration by the aquifer material (US EPA, 2008). This modification to iron nanoparticles can greatly increase the mobility of the nanoparticles in groundwater, thus increasing the effectiveness of iron nanoparticles for remediation. Of course, similar enhanced transport would not be desirable for nanoparticles that may have environmental risk implications.

Surfactants are commonly utilized in the engineering of nanoparticles to help stabilize nanoparticle suspensions. These surfactants can have a clear impact on the partitioning between aqueous, solid, and particulate phases and thus on the fate of nanoparticles in subsurface systems. In addition to engineered surfactants, many systems have natural surfactants (e.g., natural organic carbon), and some researchers have found evidence that such natural surfactants can help stabilize aqueous nanomaterial suspensions, thus enhancing subsurface transport.

Several studies have evaluated the mobility of nanosized materials in a porous medium under different conditions (Zhang, 2003; Lecoanet and Wiesner, 2004; Lecoanet et al., 2004).

2.4.3 Uptake and Accumulation of Nanomaterials in Biological Systems

Published, quantitative research on the bioavailability, uptake, and bioaccumulation of ENMs in plants and animals is scarce (Klaine et al., 2008). However, the body of research on effects of ENMs is far more developed and provides some clues as to the potential for bioaccumulation of ENMs released into the environment. In fact, the vast majority of research involving ENMs and biological systems is focused on interactions (e.g., positive effects on plant growth) and potential toxicity, especially on standard animal models such as *Daphnia magna* as well as on test organisms that will likely be exposed to ENMs through close contact (e.g., soil bacteria). Based on first principles, it is evident that organisms exposed to environmentally relevant concentrations of ENMs will be capable of accumulating these materials. Nano-sized particles—due to their size—can diffuse through cell membranes, can by engulfed by cells, or can adhere to cells. Because some ENMs are designed specifically for drug delivery purposes, it is reasonable to assume that they will interact with proteins and other cellular components and, especially, be taken up by the gut (Klaine et al., 2008). Despite the fact that little published research exists to determine how efficiently different types of organisms may accumulate and, possibly, translocate ENMs within the body, it is clear that potential interactions at the cellular level *may* allow for the relatively efficient accumulation of ENMs and, possibly, some level of magnification in the food chain.

2.5 Challenges to Modeling Nanomaterials

Predicting the behavior of ENMs in the environment requires an understanding of: (1) the potential sources of ENMs; (2) the distribution of ENMs once released into the environment; and (3) the transformations and persistence of ENMs in the environment (Lowry and Casman, 2009). Significant modeling challenges make current estimations of ENM fate highly uncertain. This section of the state-of-the-science report discusses the challenges listed below:

- Complexity of ENM transport characteristics and associated data gaps
- Variability in nanomaterial types and properties
- Limitations of current modeling approaches

- Need for near term risk management decisions.

2.5.1 Complexity of Transport Characteristics and Behaviors and Associated Data Gaps

The locations, concentrations, and properties of ENMs released to the environment will affect their distribution, concentration, and ultimately their effects on the health of receptors, including humans and ecosystems (Lowry and Casman, 2009). Two aspects of this complexity bear noting. First, as described in detail above, properties and processes that define nanomaterial transport (e.g., stability of dispersions; simultaneous chemical and particle characteristics) can be quite different from properties and processes considered in most traditional risk assessment (e.g., Henry's constants, K_d for aqueous-solid phase partitioning). Second, at each stage of modeling ENM transport, there are large uncertainties that cannot be quantified given currently available data and models. These uncertainties do not purely surround the values of traditional parameters, but they also include potentially unique causal mechanisms of transport that, as of this report, have not been fully addressed (SCENIHR, 2007). Thus, identifying the chemical and physical properties required to predict the transport of ENMs in a natural system is crucial to developing predictive exposure models. ENMs do not conform to the behavior of conventional chemicals (Lowry and Casman, 2009) and, therefore, studies must be conducted to determine the driving properties *for specific ENMs (e.g., key chemical properties) in specific environmental settings (e.g., key water quality characteristics)*. Before adequate models for ENMs can be developed, the critical properties and mechanisms must be understood and characterized.

It should be noted, however, that there is more than just a lack of knowledge surrounding properties specific to ENM transport. Grieger et al. (2009) address the issue of uncertainty in ENMs by evaluating 31 reports and papers pertaining to ENMs and environmental health and safety. The authors present a table describing each uncertainty identified. Each uncertainty is categorized into locations and sub-locations that define the lack of knowledge area within the different environmental, human health and safety aspects of ENM exposure. A few categories of uncertainties that are of importance to environmental fate and transport taken from this chart include:

- Initial concentration levels
- Release points during the ENM lifecycle (production, use, and waste)
- The form of the released ENM (agglomerates, composites, mixtures)
- Environmental processes relevant to ENMs
- Degradation
- Bioaccumulation
- Cellular uptake.

Thus, to predict or assess the risks that ENMs may pose in the environment, we must understand the sources, characteristics, transformations, and the effect on the surface properties of those materials.

2.5.2 Variability in Nanomaterial Types and Properties

Nanomaterials exist as a widely divergent array of chemicals with very different behaviors and properties. In fact, ENMs should not be considered as a single class of substances due to their extreme diversity (e.g., Hansen, 2009; Wiesner and Bottero, 2007). Due to the wide variety in ENM properties, size, morphology, chemical composition, and the even greater variability in the types of surface coatings, an understanding of ENM processes from first principles is needed before we can generalize these findings across classes or types of ENMs (Lowry and Casman, 2009). The sheer range of types and properties poses a particular challenge in terms of developing and understanding chemical behaviors of ENMs relevant to environmental transport.

2.5.3 Limitations of Traditional Risk Assessment Models

In general, conventional models used for chemical environmental fate and exposure assessment are not directly applicable in their current form for manufactured ENMs (US EPA, 2007). For example, the Estimation Programs Interface Suite (EPI Suite) has little applicability to ENMs, because it is based on equilibrium partition coefficients and does not consider the behavior of particulates (US EPA, 2009b). Even though some models (e.g., EPA's MINTEQA2) and approaches (e.g., DLVO theory) may be useful in modeling ENMs, these models/methods will need to be modified and validated to ensure that they adequately represent the chemical properties and/or transformation processes relevant to ENMs (US EPA, 2009b). Therefore, while most established models may still provide insight, their potential application is relatively narrow for ENM risk assessment purposes (Wiesner et al. 2009).

The chemical properties required by traditional risk assessment models are unlikely to be the same properties required to model the environmental transport of ENMs. Chemical and physical properties of ENMs (**Section 2.2**) are strongly related to the processes that control movement (**Section 2.3**). Therefore, typical chemical properties for predicting chemical fate and transport such as water solubility, octanol-water partition coefficient, and vapor pressure are not as important for ENMs as particle size, surface charge and surface potential (US EPA, 2009b). Metcalfe et al. (2009) produced **Table 2-2** comparing some the characteristics needed for environmental fate and transport modeling of ENMs versus conventional compounds. This evaluation further supports the consensus that established risk assessment models (and, indeed, current thinking) *must* be adapted before they can be applied reliably to predict the environmental behavior of ENMs.

Table 2-2. Comparing the Properties Needed to Model ENMs Versus Other Contaminants

Characteristic	Nanoparticles	Other contaminants
Distribution in water	Dispersivity	Solubility
Distribution in porous media	Filtration	Adsorption/desorption
Biologically availability	Sorption?	Lipophilicity
Cellular uptake	Vesicular transport?	Passive or facilitated diffusion

Table 2-2. Continued

Characteristic	Nanoparticles	Other contaminants
Toxic mechanisms	Steric hindrance, photo-chemical effects, oxidative damage, inflammation	Interactions with cellular macromolecules and receptors, narcosis
Target trophic systems	Bottom of the food chain?	Top of the food chain

2.5.4 Need for Near-Term Risk Management Decisions

A critical issue with the development of environmental fate and transport models for ENMs and their subsequent validation is the relatively long time required to gain knowledge upon which to make decisions versus the very rapid pace of nanotechnology development (Owen et al., 2009). Therefore, the development of regulations based on quantitative risk assessments (using tools including fate and transport models) will be an inherently slow governance process. Given that reliable, mechanistic ENM risk assessment may not be available for years or even decades (Grieger et al. 2009), risk managers are in need of tools over the short term to aid in the decision making process. Thus, in the absence of reliable quantitative and qualitative data or evaluation methods, novel approaches must be attempted to gain insight for near term decision making. Given this critical issue and need, **Section 4** discusses several alternative approaches that derive more from risk management and decision analysis sciences than from traditional fate and transport analysis.

Chapter 3.0
Review Methodology for Relevant Models and Methods

This section describes the methodology used to search for relevant information on the fate and transport modeling of ENMs released in the environment. **Figure 3-1** depicts the review methodology used to identify information sources that describe the state-of-the-science for exposure modeling of ENMs. **Section 3.1** presents the search strategy developed to gather information on the type of fate and transport models needed to estimate exposure concentrations for ENMs in aquatic systems. This section includes the criteria, tools, and methodology used to frame the retrieval of appropriate references and other information. **Section 3.2** describes the sources of information that we identified as particularly useful in describing the state-of-the-science for ENM exposure modeling, including key journals, reports, research centers, and informational websites. **Section 3.3** summarizes the recent reports and compendia that are relevant to the area of nanotechnology research but only peripherally related to this report.

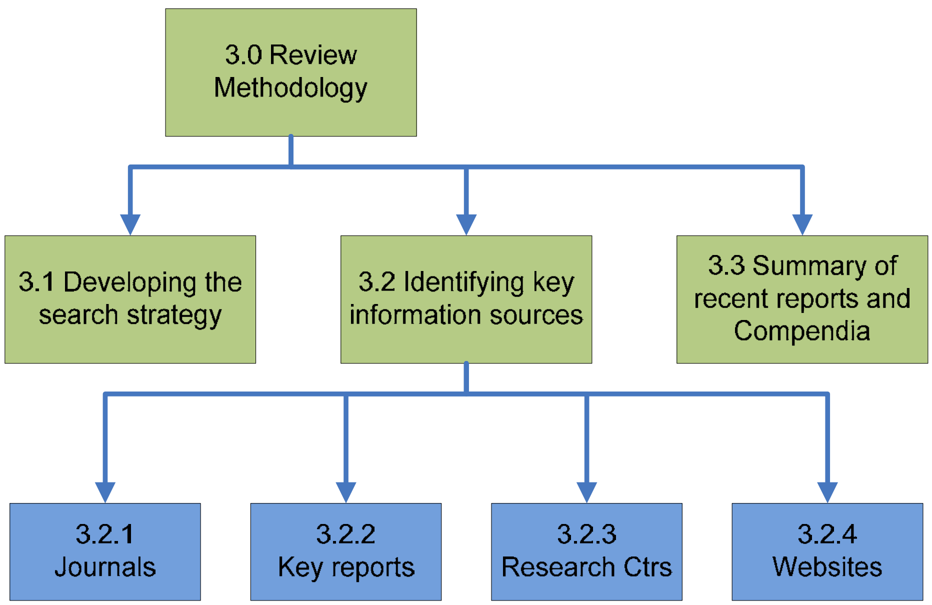

Figure 3-1. Summary of review methodology.

3.1 Developing the Search Strategy

Identifying references, published studies, and research describing the state-of-the-science in modeling the environmental fate and transport of ENMs was the primary objective of the search. We investigated a wide range of information sources, and developed an iterative search strategy to identify specific types of modeling approaches (e.g., colloid models) considered highly relevant to exposure modeling of ENMs, along with other potentially useful modeling frameworks and methods.

The search engines ScienceDirect and Google Scholar were used extensively to perform a comprehensive literature review using different combinations of search criteria as described below. Based on peer review comments, we also performed a search of the literature using the

ISI Web of Knowledge database (http://apps.isiknowledge.com/), which includes the Web of Science. The purpose of this additional search was to ensure that the use of ScienceDirect, Google Scholar, and local university searches provided adequate coverage in describing research related to the state-of-the-science.

Information pertaining to modeling ecological exposures to ENMs, particularly in aquatic systems, was further evaluated. The websites of National Science Foundation (NSF)–funded research centers were explored, as were publicly available conference proceedings and nanotechnology-related informational websites. Initially, the information search was limited to current models and approaches used in simulating fate and transport of engineered ENMs in aquatic systems. However, because technical reports that describe exposure modeling of ENMs were extremely limited, the search criteria were expanded to include other ultrafine particle types such as aerosols, polymers, and colloids. In addition, the search included information that could be relevant to fate and transport modeling (e.g., physical and chemical properties).

Elsevier's on-line technical documents service (ScienceDirect) was used as the primary source for our literature searches. ScienceDirect is one of the largest online collections of published scientific research available, containing over 9.6 million articles from over 2500 journals, and over 6,000 e-books, reference works, book series and handbooks. Searches were also conducted using the Google Scholar search engine, as well as the online libraries of North Carolina State University (http://www.lib.ncsu.edu/) and the University of North Carolina at Chapel Hill (http://www.lib.unc.edu/). As suggested above, the ISI Web of Science was used to verify that we had characterized the landscape of published literature relevant to the fate and transport, and exposure modeling of ENMs. This resource includes over 12,000 journals and more than 46 million records. The ISI Web of Science is particular helpful in identifying articles with the greatest impact to the field; for instance, the influence of a paper on the field can be determined based on the number of papers that have cited it.

We adopted a broad search strategy by incorporating combinations of key words, and this set of search criteria was used to identify models and approaches that could potentially be used to simulate the fate and transport of ENMs. **Figure 3-2** outlines the most productive search terms—by technical theme—that we used in various combinations to identify additional references.

Figure 3-2. Key search terms organized by theme.

The largest number of documents retrieved from the expanded searches pertained primarily to exposure modeling of ENMs, ENM toxicity, or safety assessments for workers involved in the manufacturing of nanoparticles (NPs). In general, we found relatively few references (compared with the results of our search) that could be considered specific to modeling the fate and transport of, or characterizing the exposure to, ENMs released into the environment.

Relevant information sources were identified from several areas of study (e.g., mining, metals transport, sedimentation processes) that had potential applicability. Understanding the key processes and research challenges specific to ENMs was critical in the assessment of models developed for other purposes. For instance, many researchers have pointed out that the environmental behavior of some ENMs is similar to colloids; thus, part of our revised search strategy focused on identifying colloidal fate and transport models for aqueous systems. In addition, research on ENMs in other fields was considered (e.g., use of iron oxide ENMs in groundwater remediation). For completeness, modeling tools were also searched across EPA research offices/programs, other federal agencies, states and EPA regions, and international trade and research organizations.

A complete listing of titles relevant to modeling the fate, transport, and exposure to ENMs released into the environment is presented in **Appendix A**. Each of these references was thoroughly reviewed, and a subset of these titles (highlighted in blue) was selected for the detailed model evaluations provided in **Appendix B**.

3.2 Identifying Key Information Sources

The search strategy produced a tremendous number of journal articles, major reports, research centers, and informational websites; however, few useful conference proceedings were identified that provided materials relevant to fate and transport modeling of ENMs. The following subsections highlight the most important information sources that we identified.

3.2.1 Journals

Table 3-1 lists the journals that produced the majority of relevant research articles that we identified. Although a much wider variety of journals was included in the search, this list presents those journals that published the highest numbers of relevant articles on modeling the fate and transport of engineered ENMs (and similarly sized particles) in aquatic systems and soils. These journals include well-established titles dealing with hydrology and environmental modeling, as well as more recently published titles focusing specifically on nanotechnology.

Table 3-1. Journals Producing the Highest Number of Relevant Studies

Journal title	First published
Water Resources Research	1965
Environmental Science and Technology	1967
Environmental Pollution	1970
Environmental Health Perspectives	1972

Table 3-1. Continued

Journal title	First published
Journal of Environmental Quality	1972
Advances in Water Resources	1977
Journal of Contaminant Hydrology	1986
Waste Management	1989
Ecotoxicology and Environmental Safety	1995
Environmental Toxicology and Chemistry	1996
Journal of Nanoparticle Research	1999
Nanomedicine: Nanotechnology, Biology, and Medicine	2005
Nanotoxicology	2007

Brief descriptions of these journals are provided below, adapted from each journal's website.

- **Water Resources Research** (WRR), 1965: a peer-reviewed scientific journal published by the American Geophysical Union (AGU). AGU states that *WRR* is an "interdisciplinary journal integrating research in the social and natural sciences of water."
- **Environmental Science & Technology** (ES&T), 1967: Published by the American Chemical Society, the journal combines magazine and research sections. The news and features section of ES&T presents objective reports and analyses of the major advances, trends, and challenges in environmental science, technology, and policy for a diverse professional audience. The research section seeks to publish papers that are particularly significant and original. The types of papers published in the research section of ES&T are research article, policy analysis, critical review, correspondence (comment/rebuttal), and correction/addition (errata).
- **Environmental Pollution**, 1970: an international journal that focuses on papers that report results from original research on the distribution and ecological effects of pollutants in air, water and soil environments and new techniques for their study and measurement. Findings from re-examination and interpretation of existing data are also included. The editors are focusing on papers that provide new insights into environmental processes and or the effects of pollutants.
- **Environmental Health Perspectives** (EHP), 1972: a monthly journal of peer-reviewed research and news published by the U.S. National Institute of Environmental Health Sciences, National Institutes of Health, Department of Health and Human Services. *EHP's* mission is to serve as a forum for the discussion of the interrelationships between the environment and human health by publishing in a balanced and objective manner the best peer-reviewed research and most current and credible news of the field.
- **Journal of Environmental Quality**, 1972: covers various aspects of anthropogenic impacts on the environment, including terrestrial, atmospheric, and aquatic systems. Emphasis is given to the understanding of underlying processes rather than to monitoring. Contributions reporting original research or brief reviews and analyses dealing with some aspect of environmental quality in natural and agricultural ecosystems are accepted from all disciplines for consideration by the editorial board.

- **Advances in Water Resources**, 1977: provides a forum for the presentation of fundamental scientific advances in the understanding of water resources systems. The scope of Advances in Water Resources includes any combination of theoretical, computational, or experimental approaches used to advance fundamental understanding of surface or subsurface water resources systems or the interaction between these systems.
- **Journal of Contaminant Hydrology**, 1986: an international journal publishing scientific articles pertaining to the contamination of groundwater. Emphasis is placed on investigations of the physical, chemical, and biological processes influencing the behavior of organic and inorganic contaminants in both the unsaturated and saturated zones. Articles on contamination of surface water are not included unless they specifically deal with the link between surface water and groundwater.
- **Waste Management**, 1989: an international journal devoted to the presentation and discussion of information on the generation, prevention, characterization, monitoring, treatment, handling, reuse and ultimate residual disposition of solid wastes, both in industrialized and in economically developing countries.
- **Ecotoxicology and Environmental Safety**, 1995: focuses on integrated mechanistic research related to short- and long-term pathways and interactions of substances and chemical mixtures in environmental systems and subsystems on their bioavailability, circulation, and assimilation in target organisms, as well as biological responses of these organisms, and damage mechanisms (endocrine disruption, genotoxicity); and on their subsequent fate in the food chain, including humans.
- **Environmental Toxicology and Chemistry**, 1996: seeks to publish papers describing original experimental or theoretical work that significantly advances understanding in the area of environmental toxicology, environmental chemistry and hazard/risk assessment. Emphasis is given to papers that enhance capabilities for the prediction, measurement, and assessment of the fate and effects of chemicals in the environment, rather than simply providing additional data.
- **Journal of Nanoparticle Research**, 1999: is an academic journal published by Springer. It focuses mainly on physical, chemical and biological phenomena and processes in structures of sizes comparable to a few nanometers. It covers the synthesis, assembly, transport, reactivity, and stability of nanostructures and devices obtained via precursor NPs, in various fields such as physics, chemistry, biology and health care.
- **Nanomedicine: Nanotechnology, Biology, and Medicine**, 2005: presents theoretical and experimental research results related to nanoscience and nanotechnology in life sciences, including Basic, Translational, and Clinical research, and commercialization of results. Article formats include Communications, Original Articles, Reviews, Perspectives, Technical and Commercialization Notes, and Letters to the Editor. In addition, regular features on our website will address commercialization, funding opportunities, and societal, Public Health, and ethical issues of nanomedicine.
- **Nanotoxicology**, 2007: is the first peer-reviewed academic journal devoted entirely to the publication of research that addresses the potentially toxicological interactions between nano-structured materials and living matter. The journal publishes the results of studies that enhance safety during the production, use and disposal of ENMs.

3.2.2 Reports

The reports shown in **Table 3-2** were produced by governmental agencies and significant research institutions.

Table 3-2. Major Reports on ENM Research Relevant to Environmental Exposure Modeling

Report title	Date	Institute	Author
Engineered Nanoparticles: Review of Health and Environmental Safety (ENRHES)	2009	Edinburgh Napier University, EU Joint Research Center, Institute for Occupational Medicine, Technical University of Denmark	Stone, V. (project coordinator) of Edinburgh Napier University
EMERGNANO: A review of completed and near completed environment, health and safety research on ENMs and nanotechnology	2009	UK Department for Environment, Food and Rural Affairs (DEFRA)	Institute for Occupational Medicine
Nanomaterial Research Strategy	2009	US EPA	Morris, J., Wentsel, R. (US EPA)
Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered ENMs	2009	National Institute for Occupational Safety and Health (NIOSH)	NIOSH
Sampling and Analysis of ENMs in the Environment: A State-of-the-Science Review	2008	US EPA	Varner, K.
Environmental Fate and Ecotoxicity of Engineered Nanoparticles	2007	Norwegian Pollution Control Authority	Bioforsk
Nanotechnology White Paper	2007	US EPA	Nanotechnology Work Group (US EPA)
Nanotechnology: A Research Strategy for Addressing Risk	2006	Woodrow Wilson International Center for Scholars	Maynard, A.

Brief descriptions of the reports are provided below, adapted from the executive summary.

- **Engineered Nanoparticles:** Review of Health and Environmental Safety (ENRHES), 2009: presents a comprehensive and critical scientific review of the health and environmental safety of four classes of ENMs: fullerenes, CNTs, metals and metal oxides. The review considers sources, pathways of exposure to the health and environmental outcomes of concern, followed by a risk assessment based upon this information. The report includes an illustration of the state-of-the-art as well as on-going work, while identifying knowledge gaps in the field. Prioritized recommendations have been developed and set in the context of informing policy makers in the development of methods to address exposure as it relates to the potential hazards posed by engineered NPs, and in the development of appropriate regulation.
- **IOM's EMERGNANO project for UK Department for Environment, Food and Rural Affairs (DEFRA)**, 2009: this project involved a detailed review and analysis of research carried out worldwide on Environment, Health, and Safety aspects of engineered NPs, including issues relating to hazard, exposure and risk assessment and regulation,

and made an assessment of how far 18 of 19 Research Objectives from this report's predecessor have been met and which gaps still remain to be filled.

- **US EPA's Nanotechnology Research Strategy**, 2009: The purpose of the Nanomaterial Research Strategy is to guide the EPA's Office of Research and Development's program in conducting focused research to inform ENM safety decisions that may be made under the various environmental statutes for which EPA is responsible. This report focuses on four areas that take advantage of EPA's scientific expertise as well as fill gaps not addressed by other organizations. The four research themes are: (1) Identifying sources, fate, transport, and exposure, (2) Understanding human health and ecological effects to inform risk assessments and test methods, (3) Developing risk assessment approaches, and (4) Preventing and mitigating risks.
- **NIOSH, Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered ENMs**, 2009, this report aims to provide an overview of what is known about the potential health hazards of engineered NPs and measures that can be taken to minimize workplace exposures. It provides a detailed list of potential health concerns, reviews numerous related studies, and offers a number of recommendations to improve safety regulations and monitoring.
- **US EPA's State-of-the-Science Review**, 2008: this state-of-the-science review was undertaken to identify and assess currently available sampling and analysis methods to identify and quantify the occurrence of ENMs in the environment. The environmental and human health risks associated with ENMs are largely unknown, and methods needed to monitor the environmental occurrence of ENMs are very limited or nonexistent. Because this research is current and ongoing, much of the applicable information is found in gray literature (e.g., conference proceedings, communications with research scientists and other experts).
- **Norwegian Pollution Control Authority, Environmental Fate and Ecotoxicity of Engineered Nanoparticles**, 2008: This report is an overview of the scientific knowledge on potential negative effects that engineered NPs may have on the environment. So far, scientific evidence show that some NPs have toxic effects under laboratory conditions, but practically nothing is known about their mobility and uptake in organisms under environmental conditions. This report was written by researchers at Bioforsk Soil and Environment.
- **US EPA's Nanotechnology White Paper**, 2007: the purpose of this paper is to inform EPA management of the science needs associated with nanotechnology, to support related EPA program office needs, and to communicate these nanotechnology science issues to stakeholders and the public. The Nanotechnology Research Framework outlines how EPA will strategically focus its own research program to provide key information on potential environmental impacts from human or ecological exposure to ENMs in a manner that complements other federal, academic, and private-sector research activities.
- **Woodrow Wilson International Center for Scholars, Nanotechnology: A Research Strategy for Addressing Risk**, 2006: this report addresses the current state of nanotechnology risk research and what needs to be done to help ensure the technology's safe development and commercialization. A strategic research framework is developed that identifies and prioritizes what the author believes are the critical short-term issues.

Recommendations are made on how a viable strategic research plan might be implemented.

3.2.3 Research Centers

We identified several leading U.S. research centers that are at the forefront of studies on the behavior of ENMs in the environment. Each of these research centers are the recipients of grants from the National Science Foundation and/or the EPA, and are performing cutting edge research on a variety of technical issues central to understanding the fate and transport characteristics of ENMs in the environment. We recognize that there are also other research centers in the U.S. as well as international research centers (especially in the EU) that are involved in ENM research; however, our search strategy did not identify other centers (domestic or international) engaged in significant research that was specific to environmental fate and transport modeling of ENMs in aquatic systems. In addition, the intent was to identify centers that focused on the environmental behavior of ENMs rather than on characterizing ENM properties or developing engineering applications for nanomaterials. **Table 3-3** lists the university and the name of the research center, and provides a link to the center's website.

Table 3-3. Key Research Centers for Nanotechnology Research

Academic Institution	Research Center	Web Address
Duke University	Center for Environmental Implications of NanoTechnology (CEINT)	http://www.ceint.duke.edu/
Rice University	Center for Biological and Environmental Nanotechnology (CBEN)	http://cben.rice.edu/
University of California, Los Angeles	University of California Center for Environmental Implications of Nanotechnology (UC CEIN)	http://cein.cnsi.ucla.edu/pages/

Brief descriptions of each research center are provided below, adapted from the center's website.

- **Duke University's CEINT** was created in 2008 with funding from the National Science Foundation and the US EPA. As described on its website, CEINT is elucidating the relationship between a vast array of ENMs and their potential environmental exposure, biological effects, and ecological consequences. Headquartered at Duke University, CEINT is a collaboration between Duke and a number of leading universities and researchers (comprehensive list found here: http://www.ceint.duke.edu/participating-institutions). CEINT performs fundamental research on the behavior of nano-scale materials in laboratory and complex ecosystems. Research includes all aspects of ENM transport, fate and exposure, as well as ecotoxicological and ecosystem impacts. CEINT is developing risk assessment models to provide guidance in assessing existing and future concerns surrounding the environmental implications of ENMs. This address provides a detailed list of CEINT's partners and participating institutions:
- **CBEN's** mission is to discover and develop ENMs that enable new medical and environmental technologies. The mission is accomplished by the following:

  - Fundamental examination of the wet/dry interface between ENMs, complex aqueous systems, and ultimately our environment (Theme 1).
  - Engineering research that focuses on multifunctional NPs that solve problems in environmental and biological engineering (Themes 2, 3).
  - Educational programs that develop teachers, students, and citizens who are well informed and enthusiastic about nanotechnology.
  - Innovative knowledge transfer that recognize the importance of communicating nanotechnology research to the media, policymakers, and the general public.

  The Center's research focuses on investigating and developing nanoscience at the wet/dry interface. Water, the most abundant solvent present on Earth, is of unique importance as the medium of life. The Center's research activities explore this interface between ENMs and aqueous systems at multiple length scales, including interactions with solvents, biomolecules, cells, whole-organisms, and the environment. These explorations form the basis for understanding the natural interactions that ENMs will experience outside the laboratory, and also serves as foundational knowledge for designing biomolecular/ENM interactions, solving bioengineering problems with nanoscale materials, and constructing nanoscale materials useful in solving environmental engineering problems.

- **UC CEIN** is the sister center to Duke's CEINT. Headquartered at the University of California, Los Angeles (UCLA), it includes the University of California at Santa Barbara and other UC partners. According to UC CEIN's website, UC CEIN will explore the impact of libraries of engineered ENMs on a range of cellular life forms, organisms and plants in terrestrial, fresh water and sea water environments. By being able to predict which ENM physicochemical properties are potentially hazardous, the UC CEIN will be able to provide advice on the safe design of engineered ENMs from an environmental perspective. While UCLA serves as the lead campus for the UC CEIN, researchers from a range of other institutions and organizations are involved in the UCLA-based UC CEIN research, and a comprehensive list of domestic and international partners may be found here: http://cein.cnsi.ucla.edu/pages/institutions.

3.2.4 Informational Web Sites

The publicly-available websites shown in **Table 3-4** were identified because they provided valuable information related to fate and transport of engineered ENMs in aquatic ecosystems. The table provides a brief summary of their mission along with the current web address.

Table 3-4. Publically Available Websites Providing Valuable Information ENM Exposure Modeling

Website	Mission	Web Address
National Nanotechnology Initiative (NNI)	coordinate Federal nanotechnology research and development	http://www.nano.gov/
International Council on Nanotechnology (ICON)	improve communication between stakeholders involved with risk assessment and research	http://icon.rice.edu/
NanoRISK	newsletter addressing nanotechnology risk assessment	http://www.nanorisk.org/

Table 3-4. Continued

Website	Mission	Web Address
NanoScienceWorks	not-for-profit portal for the nanoscience research community	http://www.nanoscienceworks.org/
Nanotechnology Now (NN)	created to serve the information needs of business, government, academic, and public communities	http://www.nanotech-now.com/
Nanowerk	serve as portal for nanotechnology and nanosciences; provide links and editorial content	http://www.nanowerk.com/
Project on Emerging Nanotechnologies	ensure that risks are minimized, consumer engagement remains strong, potential benefits realized	http://www.nanotechproject.org/

Brief descriptions of these websites are provided below, adapted from each website.

- http://www.nanoscienceworks.org/

NanoScienceWorks.org is a not-for-profit community portal for the nanoscience research community. The website provides a comprehensive variety of nanotechnology and nanoscience-related information, in addition to an encyclopedia and a free monthly newsletter.

"NanoScienceWorks.org serves the nano community as a gateway to the news, journals, books, and articles that support and drive nano research and development. We invite you to explore these resources, view our slidecasts, and join our networking database of nano-involved people and institutions from around the world."

- http://icon.rice.edu/

The creation of a sustainable nanotechnology industry requires meaningful and organized relationships among diverse stakeholders. The International Council on Nanotechnology (ICON) aims at providing such interactions for a broad set of members. Managed by Rice University's Center for Biological and Environmental Nanotechnology, ICON activities promote effective nanotechnology stewardship through risk assessment, research and communication. By pooling the resources of the nanotechnology industry, government and non-government organizations and academia, ICON can cost-effectively provide a wide range of synergistic projects that serve the interests of all stakeholders. CBEN provides a financial and administrative structure for ICON, such that ICON members are also members of CBEN.

- http://www.nano.gov/

The National Nanotechnology Initiative (NNI) is the program established in fiscal year 2001 to coordinate Federal nanotechnology research and development. The NNI provides a vision of the long-term opportunities and benefits of nanotechnology. By serving as a central locus for communication, cooperation, and collaboration for all Federal agencies that wish to participate, the NNI brings together the expertise needed to guide and support the advancement of this broad and complex field.

- http://www.nanowerk.com/

Nanowerk is committed to educate, inform and inspire about nanosciences and nanotechnologies. As the leading nanotechnology and nanosciences portal, nanowerk.com delivers useful, entertaining and cutting-edge information from all things nano. Nanowerk has become the premier nanotechnology portal due to the depth, rich scope and relevance of our unique editorial content and the comprehensive resources that we put at users' fingertips. Editorial content Scientists appreciate the publicity they receive through our articles and in turn help spread the word about Nanowerk among their colleagues and scientific communities. On average Nanowerk run between 70-100 news articles every week. T news section is separated into *Business News* and *Research & General News*. Nanowork also produces a newsletter deals explicitly with the risks involved in nanotechnology. “Much of nanotechnology today is about producing nanoscale particles that, due to their size, have significantly more catalytic active surfaces. [This newsletter tries] to support a debate on the very real issues that we are facing today: the fact that engineered ENMs such as carbon nanotubes or titanium dioxide particles are finding their way from scientists’ laboratories into commercial products and we don’t understand the risks they pose to health and environment.” *Nanorisk* is a bi-monthly newsletter published by Nanowerk LLC.

- http://www.nanotechproject.org/

The Project on Emerging Nanotechnologies was established in April 2005 as a partnership between the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts. The Project is dedicated to helping ensure that as nanotechnologies advance, possible risks are minimized, public and consumer engagement remains strong, and the potential benefits of these new technologies are realized. The Project on Emerging Nanotechnologies collaborates with researchers, government, industry, NGOs, policymakers, and others to look long term, to identify gaps in knowledge and regulatory processes, and to develop strategies for closing them.

- http://www.nanotech-now.com/

Nanotechnology Now (NN) covers future sciences such as Nanotechnology, Molecular Nanotechnology (MNT), MicroElectroMechanical Systems (MEMS), NanoElectroMechanical Systems (NEMS), Nanomedicine, Nanobiotechnology, Nanoelectronics, Nanofabrication, Computational Nanotechnology, Quantum Computers, and Artificial Intelligence. NN was created to serve the information needs of business, government, academic, and public communities. And with the intention of becoming the most informative and current free collection of nano reference material. We will cover: related future sciences, issues, news, events, and general information, and make this a place to come for information, stimulating debate, and research info.

- http://www.nanorisk.org/

This newsletter deals explicitly with the risks involved in nanotechnology. "Much of nanotechnology today is about producing nanoscale particles that, due to their size, have significantly more catalytic active surfaces. [This newsletter tries] to support a debate on the very real issues that we are facing today: the fact that engineered ENMs such as carbon nanotubes or titanium dioxide particles are finding their way from scientists' laboratories into commercial products and we don't understand the risks they pose to health and environment." *Nanorisk* is a bi-monthly newsletter published by Nanowerk, LLC.

3.3 Summary of Recent Reports and Compendia

As compared to chemicals in their conventional form, the unique properties of ENMs have led to concerns about the potential health and ecological risks that might be associated with exposure to ENMs following environmental release. Given the rapid growth in the manufacture and use of ENMs, there have been a number of recent research initiatives and published reports that focus on developing basic information about ENMs. In general, these reports fall into one of the following four categories:

1. Reports that characterize the basic physical and chemical properties of ENMs
2. Reports that address aspects of modeling (e.g., particle transport) relevant to the predictive risk assessment of environmental releases of ENMs
3. Reports that summarize the state of current knowledge on the health and environmental risk assessment of ENMs
4. Reports that propose governance frameworks for the handling and safe management of ENMs.

The first category covers a wide range of research, much of which is geared towards the manufacturing aspects of ENMs. Although this information on ENMs is critical to fate and transport modeling, it was not the focus of this effort and, to some degree, was included in EPA's state-of-the-science review on sampling and analysis of ENMs in the environment (US EPA, 2008). As discussed in Section 1, the second category was the primary focus of this report, and the results of the model reviews are presented in **Sections 4.2** and **4.3**. **Sections 3.3.1** and **3.3.2** summarize recent reports and compendia that fall into the last two categories. **Section 3.3.3** addresses recent reports and compendia that pertain to the risk assessment of ENMs but were beyond the scope of this report.

3.3.1 Summary Reports on the Current State of Knowledge

This section describes several recent articles on the health and environmental risk assessment of ENMs that provide significant insight into the current state of risk assessment science as it pertains to ENMs. **Table 3-5** lists selected articles that we believed provide the most salient discussion of issues, uncertainties, and available data for the risk assessment of ENMs. It should be emphasized, again, that ENMs cover a wide range of compounds and that our use of this term should not be interpreted as a science-based simplification of nanoscale materials. Rather, it is a convention adopted for the purposes and readability of this report.

Table 3-5. Summary Reports on ENM Research Relevant to Environmental Exposure Modeling

Report title	Date	Author
The known unknowns of nanomaterials: Describing and characterizing uncertainty within environmental, health, and safety risks	2009	Grieger et al.
Redefining risk research priorities for nanomaterials	2010	Grieger et al.
Nanomaterial risk assessment and risk management: Review of regulatory frameworks	2009	Linkov, I., Satterstrom, F.K.
Decreasing Uncertainties in Assessing Environmental Exposure, Risk, and Ecological Implications of Nanomaterials	2009	Wiesner et al.

- **Grieger et al. (2009)** address the shortfalls surrounding the modeling of ENMs by identifying the uncertainties associated with these models. By discovering these known unknowns, the paper intends to generate a pathway to shrink the knowledge gaps that currently persist in the modeling of ENMs. The article identifies 31 reports and articles published by leading scientists and authorities for ENMs, classifying the uncertainties addressed in each report and presenting them in a table that categorizes each uncertainty with respect to environmental health and safety. From the assessment, the article concludes the current level of knowledge to be in an early state in need of additional studies to decrease knowledge gaps. The article thus estimates that current quantitative risk assessments may produce premature results. Lastly, the article recommends that the focus of the research be given to the assessment and development of test procedures and equipment to fully characterize ENMs so that uncertainties will be most effectively reduced in the near term.
- **Grieger et al. (2010)** discuss the recent advancement in the risk assessment approach for ENMs. The authors argue that due to the timeframe for the current approach to responsible development of ENMs, alternative approaches must be explored. The article evaluates possible alternative approaches and adaptive evaluation frameworks (precautionary matrices, multi-criteria decision analysis, etc.) and governance frameworks (International Risk Governance Council, Environmental Defense and Dupont, etc.) currently in place. Intended for decision makers, this report suggests the need for surveillance of ENMs in light of the high levels of uncertainty with ENMs.
- **Linkov and Satterstrom (2009)** review the current ENM risk management frameworks using a regulatory pyramid. Thirteen frameworks and related documents were reviewed in all, including the USEPA white paper on nanotechnology (US EPA, 2007), DEFRA (2005), and SCENIHR (2005). The authors reviewed the frameworks by the following categories: (1) science and research aspects; (2) legal and regulatory aspects; (3) social engagement and partnerships; and (4) leadership and governance. The regulatory pyramid consists of 4 levels relating to the time frames of immediate, short term, medium term, and long term ordered from bottom to top respectively. The authors find that appropriate tools in the bottom (immediate) are largely lacking and recommend an adaptive framework be utilized to manage nanotechnology risk.
- **Wiesner et al. (2009**) address the uncertainties surrounding environmental exposure, risk and ecological implications of ENMs. The authors characterize these uncertainties by asking 4 questions concerning: (1) ENM properties and environmental conditions that

control the spatial and temporal distribution of ENMs in the environment; (2) fundamental differences between natural, incidental and manufactured ENMs; (3) nano effects on bioavailability, toxicity, and other environmental end points; and (4) effects ENMs may have on ecosystems; The authors then use the findings from these 4 questions to suggest methods for conducting risk assessments of emerging ENMs.

3.3.2 Governance Frameworks

This section summarizes recent proposals to govern the production and risk management of ENMs in the face of significant uncertainty due to a lack of research data on the environmental behavior and effects of ENMs. Renn (2008) define risk governance as a process that includes the totality of actors, rules, conventions, processes and mechanisms concerned with how relevant risk information is collected, analyzed and communicated, and how management decisions are taken. **Table 3-6** lists the articles and reports that represent the most recent governance proposals.

Table 3-6. Governance Frameworks on the Production of Nanomaterials

Report title	Date	Author
Essential features for proactive risk management	2009	Murashov and Howard
Strategic approaches for the management of environmental risk uncertainties posed by nanomaterials	2009	Owen et al.
Moving toward exposure and risk evaluation of nanomaterials: challenges and future directions	2009	Thomas et al.
The Framing Nano Governance Platform: A New Integrated Approach to the Responsible Development of Nanotechnologies	2009	Widmer et al.

- **Murashov and Howard (2009)** propose a proactive approach to the management of occupational health risks based on six guidelines. The authors suggest first to utilize qualitative risk assessments based on expert judgments and extrapolations from existing data for similar materials. Secondly, develop strategies that quickly adapt to accumulating risk assessment information and to refine risk management requirements. The authors promote the ISO (International Organization for Standardization) Concept Database, which aims to update risk databases in real time to aid in decision making. The third guideline is to embody an appropriate level of precaution due to the lack of qualitative risk assessment because of the amount of uncertainty present. The fourth guideline is to generate global governance so that risk management is equivalent across the spectrum of emerging technology firms. The fifth guideline suggests the ability to elicit strong voluntary cooperation among firms. Lastly, the authors suggest that there be a high level of stakeholder involvement based on the belief that involving all stakeholders will broaden the knowledge of potential benefits and risks as they pertain to ENMs and their production.
- **Owen et al. (2009)** identifies one area of uncertainty surrounding the modeling of ENM—the complexity of their behavior in natural systems. The article then outlines two methods to address this issue: (1) a hazard-driven approach; and (2) an exposure-driven approach. The hazard-driven approach suggests a large data gathering task utilizing

extensive toxicity assessments over many types of organisms using endpoints that would cover all potential exposure routes. The exposure-driven approach would focus on the development and subsequent validation of a conceptual model of exposure for the ENM of concern by utilizing a life cycle assessment that considers sources and pathways of exposure during production, use and end-of-life. The model would need to incorporate properties specific to the transport of ENMs rather than properties used for traditional chemical assessments. The article concedes that both approaches would depend on a considerable time lag between data gathering and resultant decision making based on the information obtained. Therefore, the article suggests that environmental surveillance approaches could be used in the near term to act as a safety net, but also advocates that it is not yet clear how fit for purpose this monitoring may be.

- **Thomas et al. (2009)** implicate the need for exposure assessment due to the explosive growth of nanotechnology. This call for action stresses this need as a critical factor in the risk assessment of ENMs, which is important in fostering their sustainable development. The article argues that an assessment that identifies and characterizes the contact and uptake of compounds into organisms which may result in health effects is essential in eliminating harmful chemical exposures of humans and the environment. The authors explore the avenues of exposure from a life cycle perspective, exposure metrics, and exposure assessment activities relevant to ENMs to explain the shortcomings of current efforts, as well as justify the need for more action.
- **Widmer et al. (2009)** describe the FramingNano governance platform, which was undertaken to create proposals for a workable governance platform bases on: (a) the analysis of regulatory processes of nanotechnology; (b) consultation with stakeholders to define key issues; and (c) dissemination of information on governance of nanotechnology to allow input to its development. The overall objective of the FramingNano Governance Platform is to promote responsible development of nanotechnology without hindering innovation and commercial growth. As a result, the platform proposes guidance on 4 different levels on nanotechnology development: (1) Technical and organizational – prioritizing research needs; (2) Communication and dialogue – effective information passing to aid in policy implementation; (3) Institutional – management of policy for responsible development of nanotechnologies; and (4) International harmonization – to aid in global governance. The research conducted by the FramingNano project concluded that governance and regulation of nanotechnologies is a dynamic process and must be continuously adapted as emerging scientifically relevant information becomes available.

3.3.3 Other Relevant Nanomaterial Reports and Compendia

This section (**Table 3-7**) presents other articles that may be of importance to the progression of nanotechnology risk assessment but fell outside the scope of this review (i.e., toxicology). We did not report the summaries of these reports and compendia, but recommend these articles for readers that wish to gain insight on related aspects of risk assessment.

Table 3-7. Other Relevant Reports and Compendia on the Research of Nanomaterials.

Report title	Date	Author
Factors Influencing the Partitioning and Toxicity of Nanotubes in the Aquatic Environment	2008	Kennedy et al.
Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing	2008	Baun et al.
Nanoparticles: Their potential toxicity, waste and environmental management (literature review)	2009	Bystrzejewska-Piotrowska et al.
Safety Assessment for Nanotechnology and Nanomedicine: Concepts of Nanotoxicology	2010	Oberdörster et al.

Chapter 4.0
Model Reviews

In this section of the state-of-the-science report we evaluate several modeling approaches and specific models according to their relevance and applicability for predicting ENM transport. The focus of the review is on aquatic and terrestrial systems, including transport in surface water, sediments, groundwater, and soils. The evaluation also considers biological uptake and multimedia models (air models are not considered). In addition, the focus of this review is on organic-based nanomaterials. Many of the approaches reviewed are relevant to other nanomaterials (notably metals); however, evaluation of these materials can require additional modeling tools (such as geochemical speciation modeling) that were outside the scope of this review.

Section 4.1 presents the model evaluation framework, which provides a systematic approach for reviewing information about models and is based on National Research Council guidelines (NRC, 2007). The remainder of **Section 4** presents results of the model reviews. Summary descriptions of specific models and approaches are provided in this section. **Appendix B** provides more detailed reviews for the models and approaches that show more promise for ENM transport modeling. The model reviews are divided into two main categories: fate and transport models (**Section 4.2**) and alternative approaches (**Section 4.3**).

4.1 Model/Method Evaluation Criteria

The model evaluation framework implemented for this assessment provides a systematic and consistent approach for reviewing and summarizing information about models. The review categories were developed to be consistent with the National Research Council paper, *Models in Environmental Regulatory Decision Making* (NRC, 2007). In this report, the NRC assesses how models support the EPA's environmental regulatory process. The development and application of regulatory models is described along with recommended considerations for selecting and using models to support EPA programs. The NRC document describes criteria for evaluating whether a model and its results provide a sound basis for regulatory decision making. Using the NRC document as a guide, we compiled a series of key considerations for model evaluation and organized them into the general categories used in the model reviews. **Appendix B** provides model reviews that are structured according to these categories. We have provided reviews for models that have been developed for and/or applied to ENMs as well as other models that have potential applicability (in their present form) for the evaluation of ENM transport in the environment.

Purpose and Scope. What is the model purpose? What transport media are considered (i.e., groundwater, surface water, multimedia)? What processes are simulated? What is the conceptual basis and what are the primary assumptions? What spatial and temporal scales does the model consider? What kind of results does the model produce (e.g., media concentrations, risk, probability)?

Background and History. How extensively has the model been used and applied (e.g., a single academic study versus an established model used for extensive regulatory decision making)?

What kind of peer review has the model been subjected to? Has the model been verified through comparison with other models or laboratory experimental results? Has the model been validated through comparisons with measured environmental data?

Complexity. What physical and chemical processes are considered? What is the mathematical representation (e.g., analytical or numerical solution)? How extensive are the input data requirements?

Consideration of Uncertainty. Does the model account for uncertainty and, if so, how? Is the model process based or statistical? Is the model deterministic or probabilistic? Does the model implementation include tools for sensitivity and/or uncertainty analysis?

Availability and Usability. Is a user-friendly interface available? Does the model rely on proprietary algorithms and/or user interfaces? Is the model documentation complete and transparent? Is the source code available for potential enhancements/modifications?

Applicability to ENM Behavior. Does the model consider key processes and chemical properties relevant for the specific environmental medium or media considered in determining ENM behavior (e.g., aggregation/disaggregation, attachment/detachment in aqueous systems)? How does the model account for the gaps in the data that are necessary for traditional models? How well does this model respond to updated scientifically relevant information? What kind of information can be gathered from these types of models? What interpretations can be made from the findings of these types of models?

4.2 Review of Environmental Fate and Transport Models

In this section we describe several environmental fate and transport models and their potential applicability for evaluating ENMs. The model categories considered are based primarily on NRC's review of regulatory modeling practices at EPA (NRC, 2007). There is overlap in model constructs between some of these categories. For example porous media transport mechanisms may be important both for sediments in a surface water model as well as a groundwater transport model. Nevertheless, the model categorization used in this document is consistent with the typical structure and scope of many existing environmental fate models.

Models within the following general categories are considered:

- ***Surface water models***. Most surface water quality models account for interactions between surface water and underlying sediments (e.g., sedimentation and resuspension). Thus, this category may include models that evaluate fate and transport within the water column as well as within underlying sediments.
- ***Subsurface models.*** This category includes models that simulate environmental fate within soils, the unsaturated zone (below the soil zone and above the groundwater table), and saturated groundwater.
- ***Biological uptake models.*** This category focuses on models predicting the uptake of chemicals into biological organisms and associated potential bioaccumulation.

- ***Multimedia models.*** These models account for processes and mass transfer across multiple environmental media. There is redundancy between multimedia models and the other model categories. In fact, some multimedia modeling systems explicitly include media-specific submodels (e.g., the EXAMS surface water model within the Multimedia, Multipathway, Multireceptor Exposure and Risk Assessment [3MRA] modeling system). Nevertheless, multimedia models deserve focused consideration given their extensive use in many traditional environmental risk assessments.

Within each of the model categories listed above, we have evaluated models of three types:

- ***Models specific to nanomaterials.*** These models were developed for and/or used specifically to evaluate ENM transport. The models considered were identified during the literature review documented in **Section 3**.
- ***Established regulatory models.*** Given the focus of this assessment on supporting EPA's evaluation of models for regulatory support, we have provided a discussion of several existing, established models currently used by EPA to evaluate chemical fate in the environment. In most cases, these models are not appropriate for modeling ENMs in their present form, because they do not consider critical properties and processes for ENMs. The discussion will highlight limitations of such models and modeling approaches. The regulatory models evaluated correspond to those listed in NRC's review of EPA regulatory modeling practice (NRC, 2007). Although these models represent only a subset of the available models used by EPA, they are among the most widely applied, and they are representative of typical risk assessment modeling practice by the agency.
- ***Other models***. In some cases, existing models developed for other contaminants may provide potentially useful approaches for simulating ENM environmental transport. For example, given their particulate nature, modeling approaches for colloid transport in porous media may be relevant to nanoparticles.

4.2.1 Surface Water Models

As discussed in **Section 2.4.1**, many traditional environmental fate models of chemicals in aquatic systems consider some or all of the following important processes: dissolution, volatilization, adsorption, biological uptake, photolysis, hydrolysis, and biodegradation (see **Section 2.4.1**). Less common are environmental fate models that consider processes of aggregation, attachment, and sedimentation, all processes critical to understanding and predicting the environmental fate of ENMs (**Sections 2.3** and **2.4**). Models predicting ENM behavior in aquatic environments should account for these critical processes related to particulates in natural systems. The evaluations of surface water fate and transport models in this section primarily consider whether models account for these key processes.

4.2.1.1 Surface Water Models of Nanomaterials

This section describes surface water models identified in the literature that have been developed and/or applied specifically for the evaluation of ENM fate in the environment. **Appendix B** provides more detailed reviews of each of these models.

Mackay et al. (2006) developed a stochastic probability model predicting the environmental stability of nanoparticle suspensions in aqueous solutions and the associated uncertainty. The model simulates settlement utilizing critical buoyancy properties and the Boltzmann equation. Rates of aggregation are estimated based on molecular collision and adhesion coefficients. **Appendix B** provides a more detailed review of the Mackay et al. (2006) model.

Boncagni et al. (2009) implemented an experimental study of the exchange of titanium dioxide nanoparticles between streams and streambed sediments. They evaluated the degree of aggregation and sedimentation under a range of conditions (pH and water flow velocity). They utilized the process based model of colloids in surface water systems developed by Packman et al. (2000) to interpret the results. The model was formulated based on advective pumping theory, colloid filtration, and settling. The Packman model is discussed further in **Section 4.2.1.3** and is reviewed in **Appendix B**.

Koelmans et al. (2009) performed a compartmental modeling analysis of mass transfer between surface water and sediments, considering particulate transport processes. The model estimated steady state concentrations of carbon-based nanoparticles by accounting for processes of sedimentation, aggregation, degradation, and burial in deeper sediment layers. The model assumes: (1) a distinct, mixed biologically active layer; (2) transport of manufactured carbon nanoparticles to sediment is through sedimentation; and (3) the removal of manufactured carbon nanoparticles can be modeled as a first order decay process. Their analysis suggested that concentrations of manufactured carbon-based nanoparticles in aquatic sediments will likely be negligible relative to levels of black carbon nanoparticles (incidental ENMs generated as combustion byproducts). **Appendix B** provides a more detailed review of the Koelmans et al. (2009) model.

4.2.1.2 Regulatory Surface Water Models

This section discusses several established surface water models that have been used in risk assessments to support EPA regulatory programs. The models evaluated correspond to those listed in NRC's review of EPA regulatory modeling practice (NRC, 2007). Although these models represent only a subset of the available surface water models used by EPA, they are among the most widely applied, and they are representative of typical risk assessment modeling practice by the agency.

The three reviewed models are moderate complexity, conceptual models (see **Box 4-1**). The models do consider some of the key processes characterizing particulate transport in aqueous systems, including sedimentation, resuspension, and particulate advection. However, their current applicability for predicting ENM behavior is significantly limited by lack of knowledge and lack of available, empirical data characterizing ENMs. Furthermore, it is as yet unknown whether the associated lumped-parameter formulations will be adequate for simulating the environment behavior of ENMs or whether alternative modeling constructs will be required. For example, if sufficient empirical knowledge becomes available to support model parameterization, can mass transfer between the water column and underlying sediments be adequately modeled using a lumped mass-transfer-rate formulation? Given the limited applicability of regulatory surface water models for evaluating ENMs at this time, we provide only a brief review of each model and have not included more detailed reviews of these models in **Appendix B**.

HSPF (The Hydrological Simulation Program–FORTRAN) is a modeling package for simulating watershed hydrology and water quality. HSPF adopts a basin-scale approach, incorporating pollutant source models and fate and transport in one dimensional stream channels. The model accounts for watershed hydrology, including sediment runoff processes along with in-stream hydraulic and sediment-chemical interactions. Simulation results include time series of the runoff flow rate, sediment load, and contaminant concentrations, as well as water quantity and quality. HSPF considers up to three sediment types (sand, silt, and clay) in addition to a single dissolved organic chemical and transformation products of that chemical. The model considers the following reaction processes: hydrolysis, oxidation, photolysis, biodegradation, volatilization, and sorption. The model accounts for particulate settling and potential resuspension. Resuspension is modeled based on the shear stress at the sediment water interface and the capacity to transport particulates at a particular flow. Mass transfer with sediments is modeled as sorption/desorption and deposition/scour processes. Fate and transport mechanisms within the sediments (e.g., pore water flow, bioturbation) are not modeled. HSPF has been used in hydrologic

Box 4-1. Complexity and Empiricism in Environmental Risk Assessment Modeling

Fate and transport models used in risk assessment often do not include extremely detailed, mechanistic formulations of fate processes. Rather, these models often encapsulate detailed processes using simpler formulations. One example would be a surface water model that describes the mass transfer between a water column and underlying sediments using a single mass transfer rate even though the underlying processes may be quite varied and complex (sedimentation, scouring, adsorption, bioturbation, diffusion, pumping exchange). In this case, the mass transfer rate could be considered a *lumped parameter* designed to capture the cumulative effect of a range of relevant processes. Models that adopt such an approach have been referred to as *conceptual models* in that the model provides a conceptual framework for the underlying processes (Wainright and Mulligan, 2004).

One can consider a continuum of model types from empirical models that rely only on data with no underlying conceptualization of the system (e.g., a fitted regression equation) to physical models that are based on a detailed, mechanistic and spatially explicit understanding of the underlying processes. In general, physical models are fully distributed spatially; empirical models are fully lumped with no explicit spatial representation. Conceptual models (i.e., most risk assessment fate and transport models) are typically semi-distributed, falling in the middle of the continuum between physical and empirical models.

Conceptual models may appear to compromise scientific rigor by ignoring known complexities. However, such an approach is often necessary in order to predict environmental behaviors given the typically extreme variability, complexity, and uncertainty associated with natural systems. In other words, additional scientific detail and complexity do not necessarily increase model reliability, particularly when dealing with highly variable and uncertain systems. However, it is generally not possible to make predictions using conceptual models a priori (i.e., based on theoretical considerations alone). Rather, conceptual models must be grounded in empirical evidence in order to produce realistic predictions of environmental behavior. For example, model input parameters such as mass transfer rates and reaction terms may be adjusted until model predictions are reasonably close to measured data (i.e., model calibration). In addition, conceptual models may parameterized using regressions previously developed from empirical data (e.g., correlations relating surface water volatilization rates to wind speed). Large-scale (e.g., national) risk assessments may not have sufficient available data to support model calibration; nevertheless, the model input distributions are typically based on empirical knowledge gained through laboratory experimentation and field data collection.

In summary, models often used in regulatory risk assessment are moderately complex, conceptual models. Parameterization of such models must be based on empirical evidence in order to make reliable predictions. Very limited knowledge (experimental and field data) of ENM transport is available to support the use of such modeling frameworks at this time.

and water quality evaluations, including analysis of pesticide runoff and agricultural best management practices.

WASP provides a dynamic compartment-modeling approach for aquatic systems, including both the water column as well as the underlying sediments. The model can evaluate 1, 2, and 3 dimensional systems and a variety of pollutant types, including particulates. The model considers processes of advection, dispersion, point and diffuse mass loadings and boundary mass transfers. Sediment transport processes include advection, dispersion, settling (and sedimentation), as well as erosion to the water column from the sediment layer. Example uses of the WASP model include evaluations of eutrophication, phosphorus loading, bacterial contamination, as well as PCB, VOC, and heavy metal pollution.

QUAL2K provides a relatively simple model for simulating flow and water quality in rivers and streams. The model has been used to evaluate the environmental impact of pollution discharges along rivers from point and non-point sources. The model has been used extensively to support National Pollutant Discharge Elimination System (NPDES) wastewater discharge permit applications, total maximum daily load (TMDL) studies, and environmental impact statements for proposed development. A wide range of chemical and biological pollutants within a river can be modeled, including carbonaceous biochemical oxygen demand, nitrogen and phosphorus, suspended solids, algae, pathogens, phytoplankton and detritus. Physical-chemical processes simulated by the model include water quality kinetics, chemical equilibrium, advection, dispersion, settling, and interactions with the atmosphere (re-aeration) and riverbed (sediment oxygen demand). Water quality parameters predicted throughout the modeled river domain include dissolved oxygen concentration, pH, salinity and temperature, in addition to the various pollutant quantities.

4.2.1.3 Other Surface Water Models

This section describes surface water models that appear to have potential utility for modeling ENMs but that were not developed specifically for that purpose.

Packman et al. (2000) developed a process-based model to simulate the transport of colloids in surface water systems, including the mass exchange between the water column and underlying sediments. The model accounts for particle settling and sedimentation processes as well as pumping exchange of particulates due to water flow through sediment bedforms induced by stream flow. Their formulation also considered particulate filtration in the porous bed sediments. Using their model, solute and colloid exchanges may be predicted without fitting coefficients and only requiring measurable hydraulic and particle parameters as inputs. One limitation of the model is that it does not account for changes in the particulate suspension (e.g., due to time varying pH or ionic strength). The Packman et al. (2000) model was used by Boncagni et al. (2009) to simulate the behavior of titanium dioxide nanoparticles in surface water systems (see **Section 4.2.1.1**). **Appendix B** provides a more detailed review of the model.

4.2.2 Subsurface Models

As discussed in **Section 2.4.2**, many traditional environmental fate models of chemicals in terrestrial systems consider some or all of the following important processes: dissolution, volatilization, adsorption to organic and inorganic matter, biological uptake, photolysis, hydrolysis, and biodegradation. Less common are environmental fate models that consider processes of aggregation, attachment, and sedimentation, all processes critical to understanding and predicting the environmental fate of ENMs. Models predicting ENM behavior in the terrestrial environments should account for these critical processes related to particulates in natural systems. The evaluations of subsurface fate and transport models in this section primarily consider whether models account for these key processes. Some established modeling approaches show promise for modeling subsurface ENMs, particularly colloid transport models (US EPA, 2007). **Box 4-2** provides some additional background information about subsurface colloid transport modeling.

Box 4-2. Subsurface Colloid Transport Modeling

Colloid transport is often modeled using an advection-dispersion equation modified to account for colloid attachment and detachment. The most common approach relies on CFT (also called clean bed filtration theory). This formulation accounts for first-order kinetic attachment and assumes that detachment is negligible (Tosco et al., 2009). However, experiments have shown that CFT theory is not always valid. In addition to detachment, CFT does not account for so-called blocking effects (also known as ripening), whereby a maximum, threshold concentration of colloids is able to attach to the solid. Such blocking behavior may be described using a Langmuirian isotherm approach. Other mechanisms not considered in CFT include straining and enhanced transport (see **Section 2.3.4**). In addition, CFT approaches do not typically consider the potentially strong effects of solution chemistry on colloid attachment/detachment behavior (as described by DLVO theory and its extensions). Some models have extended CFT in order to account for some of these additional processes.

4.2.2.1 Subsurface Models of Nanomaterials

This section describes subsurface models identified in the literature that have been developed and/or applied specifically for the evaluation of ENM fate in the environment. **Appendix B** provides more detailed reviews of each of these models.

Tosco and Sethi (2009) developed a one-dimensional model called MNM1D (micro and nanoparticle transport model in porous media in 1D geometry). The model considers constant or transient hydrochemical parameters (ionic strength) and describes attachment and detachment phenomena. The model accounts for multiple attachment sites, one based on linear and another based on Langmuirian isotherms (thus accounting for blocking effects as described in Box 4-2). The governing partial differential equations were solved using a finite difference solution, and the model was validated through comparison with other models (HYDRUS 1D and Stanmod). The model was developed in Matlab and may be downloaded from the website www.polito.it/groundwater/software. **Appendix B** provides a more detailed review of the Tosco and Sethi (2009) model.

Ju and Fan (2009) developed a nanoparticle transport model for use in enhanced oil recovery (EOR) applications. The proposed EOR approach involves the injection of polysilicon nanoparticles to change the solid matrix from an oil wet to a water wet system. The model includes both oil and water phases and accounts for blocking as well as permeability reduction. Thus, the model accounts for complex processes (e.g., multiphase flow, permeability reduction from particle straining). However, the model is one dimensional. Given that the purpose of this model is to support enhanced oil recovery involving multiphase flow processes, we have not performed a more detailed review of this model.

Li et al. (2008) developed a model to evaluate the transport of fullerene (C60) nanoparticles. This model accounts for nonequilibrium attachment kinetics and maximum retention capacity (site blocking). The authors developed a correlation for the maximum retention capacity allowing prediction based on flow velocity, nanoparticle size, and mean grain size of the porous medium. The authors determined that patch-wise surface charge heterogeneity on the sand grains is probably the reason that observations deviated from classical DLVO theory. They concluded that modifications to clean-bed filtration theory and accounting for surface heterogeneity are necessary to predict nC60 transport behavior in saturated porous media. **Appendix B** provides a more detailed review of the Li et al. (2008) model.

Liu et al. (2009) modeled experimental transport results for engineered multiwalled carbon nanotubes (MWCNTs) using a one-dimensional model. This model includes a new theoretical collector efficiency relationship to describe colloid attachment behavior. The model is based on traditional colloid filtration theory (CFT) modified with a site-blocking term. The model provided good agreement with experimental results. **Appendix B** provides a more detailed review of the Liu et al. (2009) model.

Cullen et al. (2010) simulated the transport of nano-fullerenes (C60) and MWCNTs using a two-dimensional finite element model. The model considered heterogeneity in permeability. The model is based on classical CFT modified with a maximum retention capacity term. Their results indicated that carbon nanotubes are more mobile than C60. This study utilized the commercially available model, COMSOL Multiphysics version 3.4a. Their results show that nanoparticle transport and maximum concentrations are very sensitive to collision efficiency factors and blocking factors (parameters controlling colloidal attachment). As these authors emphasized, accurate methods to predict these parameters from soil and nanoparticle characteristics have not been developed, especially for natural environmental conditions. **Appendix B** provides a more detailed review of the Cullen et al. (2010) model.

4.2.2.2 Regulatory Subsurface Models

This section discusses several established subsurface models that have been used in risk assessments to support EPA regulatory programs. The models evaluated correspond to those listed in NRC's review of EPA regulatory modeling practice (NRC, 2007). Although these models represent only a subset of the available subsurface models used by EPA, they are among the most widely applied, and they are representative of typical risk assessment modeling practice by the agency.

None of the three evaluated regulatory models accounts for key processes of ENM subsurface transport, including aggregation, attachment, and porous media filtering. The models therefore are not suitable in their present form for evaluating ENM transport. We have thus provided only brief reviews of these models below.

It is worth mentioning that some researchers have simulated colloid facilitated transport (see **Section 2.3.4**) using conventional porous media transport models (such as the three regulatory models reviewed in this section). For example, Contardi et al. (2001) and Vilks et al. (1998) utilized a transport model accounting only for advection, dispersion, sorption, and decay. They recognized that the model did not account for colloid behavior explicitly; however they utilized an approximate approach to decrease the degree of sorption in order to account for colloid facilitated transport. This modeling approach essentially utilizes a lumped-parameter approach to simulate complex processes (see Box 4-1). If such an approximate approach is effective for simulating ENMs, the regulatory models described in this section may have potential use. However, given the unique and complex behaviors exhibited by ENMs in porous media, it seems unlikely that this approach would provide reliable predictions for a broad range of conditions.

The **PRZM** modeling package couples a model of pesticide and nitrogen fate in the crop root zone with a variably saturated flow and transport model of the deeper unsaturated zone. The one-dimensional root zone model is solved using a finite difference approach (formulated from multiple homogeneous compartments in series). The deeper unsaturated zone model is based on a finite-element solution of Richard's equation for flow and an advection-dispersion equation for transport. PRZM accounts for processes of advection, dispersion, sorption, biodegradation (including up to two degradation products). The model also simulates surface runoff and sediment erosion, including the transport of contaminants sorbed to sediments. The model includes a Monte Carlo pre-and post-processor that supports probabilistic simulations. PRZM has been used extensively to evaluate the fate of pesticides in agricultural settings. Other than surface runoff the model does not include processes specific to particulate transport such as aggregation, attachment, and porous media filtering. Therefore, PRZM is not suitable in its current form to simulate the behavior of ENMs.

MODFLOW is a modular three-dimensional finite-difference groundwater flow model developed by the U.S. Geological Survey and first published in 1984. MODFLOW is one of the most widely used groundwater flow and transport models. Although the original version of the model only considered groundwater flow, MODFLOW's modular structure has allowed integration of many additional capabilities. The MODFLOW modeling system now includes capabilities to simulate coupled groundwater/surface-water systems, solute transport, variable-density and unsaturated-zone flow, aquifer-system compaction and land subsidence, parameter estimation, and groundwater management. The model is based on a finite difference numerical solution to the groundwater flow and transport equations. The model does not include processes specific to particulate transport such as aggregation, attachment, and porous media filtering. Therefore, MODFLOW is not suitable in its current form to simulate the behavior of ENMs in the environment.

BIOPLUME is a two-dimensional finite difference model utilized to simulate processes of natural attenuation of organic contaminants in ground water. Attenuation processes considered include advection, dispersion, sorption, and biodegradation. BIOPLUME was developed from the U.S. Geological Survey solute transport model MOC. The model considers the fate and transport of the contaminant as well as several aerobic and anaerobic electron acceptors, including oxygen, nitrate, sulfate, iron (III), and carbon dioxide. Three kinetic formulations are available to simulate biodegradation reactions, including first-order decay, instantaneous reaction, and Monod kinetics. BIOPLUME does not include processes specific to particulate transport such as aggregation, attachment, and porous media filtering. Therefore, BIOPLUME is not suitable in its current form to simulate the behavior of ENMs in the environment.

4.2.2.3 Other Subsurface Models

This section describes subsurface models that appear to have potential use for modeling ENMs but that were not developed specifically for that purpose. Several researchers have developed modeling approaches for simulating colloid transport in porous media. We have provided a brief summary of several of these studies below. More detailed reviews are provided in **Appendix B** for the established models TOUGH2 and HYDRUS.

Corapcioglu and Choi (1996) developed a one-dimensional model describing colloid transport in unsaturated porous media with four phases (aqueous, air, solid matrix, and colloid). They concluded that the air–water interface could strongly limit colloid transport due to colloid attachment to the air–water interface. Johnson et al. (2007) incorporated geochemical heterogeneity and random sequential deposition dynamics. Sun et al. (2001) developed a two-dimensional colloid transport model for heterogeneous porous media. Ryan et al. (1999) considered the importance of the geochemical environment on colloid attachment/detachment behavior by developing a two-dimensional model accounting for physical and geochemical heterogeneity. Bradford and Toride (2007) attempted to account for non-CFT behavior using a conventional advection-dispersion equation (ADE) model with first order kinetic deposition and release; they allowed some parameters to vary stochastically in successfully simulating experimental results. Bekhit and Hassan (2005) developed a 2D colloid transport model accounting for potentially facilitated and retarded colloid transport.

Moridis et al. (2003) utilized the **TOUGH2** (Pruess, 1991) model to develop three-dimensional simulations of a proposed nuclear waste disposal facility and associated colloid transport. This effort accounted for colloid transport using the EOS9nT module (Moridis et al., 1999). **Appendix B** provides a more detailed review of the EOS9nT module of TOUGH2.

HYDRUS is a software package for simulating water, heat, and solute movement in two- and three-dimensional variably saturated media. The model includes several optional mechanisms of colloid transport as documented in Šimůnek et al. (2006). **Appendix B** provides a more detailed review of the HYDRUS model.

4.2.3 Bioaccumulation Models

Although the focus of this state-of-the-science review was on fate and transport models, we recognize that the bioaccumulation of ENMs may, for some materials, represent a significant exposure pathway. Therefore, we include this short summary of bioaccumulation models for completeness, focusing primarily on organic chemicals. It should be noted that there is a considerable body of research and attendant models available to estimate tissue concentrations of organic chemicals, and the past few years have seen considerable advances in our ability to predict uptake and accumulation of metals.

There are several types of mathematical modeling approaches that have been developed and used in predicting exposure concentrations in biota, especially in aquatic systems. These approaches can be classified as (1) quantitative structure-activity models, (2) mass balance models, and (3) food web bioaccumulation models. The distinction among these models are certainly blurred because QSAR elements are found—either explicit or imbedded—in all bioaccumulation models and, similarly, kinetics (i.e., absorption, distribution, metabolism, and elimination [ADME]) tend to be represented in most models, often using the log of the octanol-water partition coefficient as a surrogate; nevertheless, it is useful to organize the types of predictive bioaccumulation models into these categories.

Based on this review, no models or modeling approaches were identified that (1) have been applied to ENMs or, (2) because of their theoretical underpinnings, could *readily* be used to predict the bioaccumulation of ENMs in aquatic biota. Therefore, this section summarizes each approach and provides a brief discussion of the potential relevance and applicability to ENM bioaccumulation. Given the plethora of published research on the development and validation of models to predict the uptake and accumulation of conventional chemicals, we identified a handful of articles and reports that provide an excellent overview of methods as well as the uncertainties associated with predictive bioaccumulation models. The primary sources of information identified for this review were

- Bioaccumulation Assessment Using Predictive Approaches (Nichols et al., 2009)
- Uncertainties in ecological, chemical, and physiological parameters of a bioaccumulation model: Implications for internal concentrations and tissue-based risk quotients (DeLaender et al., 2010)
- Evaluation of Chemical Bioaccumulation Models for Aquatic Ecosystems – Final Report (Aqua Terra, 2004).

QSAR Models. The earliest approaches to predict chemical concentrations in aquatic organism is based on the relationship between an organism's BCF[4] and the log of the *n*-octanol-water partition coefficient (log K_{ow}). As pointed out by Nichols et al. (2009), a curvilinear relationship is obtained when plotting the BCF versus the log K_{ow} up to a log K_{ow} value of roughly 6. The use of log K_{ow} as a predictor of bioconcentration potential is based on the behavior of hydrophobic organic chemicals, namely, the partitioning of hydrophobic organics into the lipid tissue of animals. Because *n*-octanol tends to be a useful surrogate for lipid, this approach has proven to be very useful within the range of chemicals for which uptake across the gills (versus uptake through the food web) tends to be the driving exposure route. More recent development of QSAR algorithms adjusts the baseline (i.e., the BCF based strictly on the log K_{ow}) by chemical-specific attributes such as ionizability. This same type of approach has proven to be extremely useful in predicting toxicity for chemical classes with similar modes of action (MOA) such as organic chemicals that cause adverse effects via narcosis (see, for example, Netzeva et al., 2007).

[4] For the purposes of this discussion, the BCF is defined simply as the ratio of the chemical concentration in fish per unit mass over the chemical concentration in water per unit volume.

However, because these QSAR methods are often derived from empirical studies, and because they rely heavily on the assumption that *n*-octanol is an appropriate surrogate for lipid (implying that the chemical partitions to lipid preferentially), these methods are unlikely to support predictions for ENMs without considerable research demonstrating how ENMs partition from the gut into other tissues following exposure. It is reasonable to assume that the mechanism for partition for many ENMs (certainly quantum dots) is very different than the mechanism for conventional organic chemicals and, therefore, QSAR approaches based on the log K_{OW} are unlikely to produce reliable predictions without extensive study into the actual mechanisms that drive partition of ENMs.

Mass Balance Models. These types of models predict bioaccumulation in various body parts, in essence, by representing processes associated with chemical uptake (e.g., the amount of water that passes across the gill) and elimination (e.g., the dilution of chemical mass associated with growth of the animal). The model conceptualizes the animal as one or more compartments (or boxes) and the concentration of chemical in each box is a function of the processes that affect the throughput of the chemical mass (Aqua Terra, 2004). In this engineering type approach, some mass of chemical enters the box (e.g., parent compound that is not biotransformed), some mass of chemical remains in the box (i.e., accumulation), and some mass of chemical leaves the box (i.e., elimination). Most of these approaches are developed to solve the equation for steady-state conditions and, therefore, supporting studies must demonstrate that steady state has been achieved to provide reliable data for model validation. Naturally, the development of suitable study data must address ADME and, as Nichols et al. (2009) point out, there is already a need to improve the representation of ADME processes for conventional chemicals. The authors point out that metabolism has long been a significant source of uncertainty for hydrophobic chemicals (consider the importance of metabolism in predicting the tissue concentrations of polycyclic aromatic hydrocarbons [PAHs]). Given the hydrophobicity of certain classes of ENMs (e.g., low solubility of fullerenes), significant research may be required before a mass balance approach may be applied reliably to ENMs. However, mass balance approaches may be developed that *simplify* the ADME paradigm by eliminating processes that are not relevant to ENMs (e.g., certain elimination mechanisms may not be relevant for ENMs that bind strongly to cellular proteins).

Food Web Bioaccumulation Models. Whereas mass balance models are designed to predict uptake and accumulation from water only exposures, food web models account for the exposure to chemicals via water passing across the gills as well as through the diet (i.e., consuming prey species that have accumulated some level of the chemical). These types of models can be limited to aquatic food webs or they can be extended to terrestrial organisms that consume aquatic animals. The primary difference between the mass balance class of models and food web models is that food web models consider (and solve for, mathematically) multiple trophic levels simultaneously. For chemicals that are efficiently metabolized by lower trophic level organisms the predicted tissue concentrations may approximate the predictions generated using a mass balance approach because water is the dominant exposure pathway (i.e., the chemical may not biomagnify up the food chain). In contrast, if dietary exposure to a chemical is dominant, food web models will produce a much higher estimate of tissue concentrations than a mass balance model that only considers water only exposures. As suggested above, the food web class of models is also based on kinetics principles (i.e., ADME), and require suitable studies to measure parameters related to the chemistry (e.g., log K_{ow}), ecology (e.g., nonlipid organic carbon in detritus), and physiology (e.g., diffusion resistance for uptake) to produce useful predictions (De Laender et al., 2010). This strongly suggests that, for food web models to be considered for ENMs, substantial research would be needed across all trophic levels.

It should be noted that, although these classes of bioaccumulation models may not be immediately useful in predicting tissue concentrations in aquatic ecosystems for the purposes of exposure assessment, the theoretical bases of these approaches have been developed and validated over many years and, in general, model performance has been considered appropriate to support risk management decisions. A variety of models have been created and used for both organic chemicals and metals (e.g., EPA's Bioaccumulation and Aquatic System Simulator, or BASS, Barber, 2008) and, therefore, there is significant potential for further development of these concepts to represent processes that are specific to ENM behavior in aquatic ecosystems.

4.2.4 Multimedia Models

Multimedia models treat various environmental media (e.g., surface water, groundwater and atmosphere) as an integrated system, synthesizing information about chemical partitioning, reaction, and intermedia transport. Multimedia models have been used to estimate regional and global contaminant migration based on mass balance relationships (Fenner et al., 2005). Multimedia models have also been used to assess transport at more local scales, including risk assessments of point contamination sources (e.g., industrial sources of hazardous waste). This section reviews several multimedia models that have been developed specifically to evaluate ENMs (**Section 4.2.4.1**). In addition, several multimedia modeling frameworks established within the risk assessment community are discussed (**Section 4.2.4.2**).

Many multimedia models are compartmental models based on a mass balance formulation. Such models estimate the transport of material through (often homogeneous) compartments during the life cycle of a chemical and may include the following steps: (1) characterize the source and production volumes of material (compounds or chemicals); (2) estimate the emissions of material to environmental compartments (air, sediment, soil, surface water, etc.); (3) specify the fate in the environment; and (4) derive distributions of predicted environmental concentrations (PECs) and predicted no effect environmental concentrations (PNECs) for the studied material.

One approach to calculate PECs and PNECs is material flow analysis (MFA) (also known substance flow analysis, SFA), which is a method of analyzing the flows of material or substance in a well-defined system. Generally, the goal of a MFA is to obtain an understanding of the material flows, calculate indicators, and develop strategies and measures for improving the material flow system. MFA can be used to determine flows to and amounts of materials within the studied environmental compartments. It is also possible to extend MFA into a probabilistic material flow analysis (PMFA), in which the goal is to derive probability distributions of PECs. The PMFA is designed to calculate concentrations of possible contaminants in environmental compartments and life stages associated with these contaminants.

The goal of many multimedia modeling analyses is to estimate PECs of potential hazards as well as PNECs such that the risk quotient (PECs/PNECs) can be calculated. From this risk quotient, risk managers can determine which chemicals are at greater risk (typically a risk quotient >1). Sensitivity and uncertainty analysis (when available) can also be beneficial in the development of intervention strategies for the chemicals associated with higher risk.

4.2.4.1 Multimedia Models of Nanomaterials

This section describes multimedia models identified in the literature that have been developed and/or applied specifically for the evaluation of ENM fate in the environment. Each of the models will be further reviewed in **Appendix B**.

Boxall et al. (2007a) developed a deterministic model by deriving dilution equations predicting the environmental concentrations of ENMs in surface water, sludge, and soil. This model determines the PECs of specific ENMs after a life cycle that includes production, use, emission, and disposal. The model uses estimations and data values for parameters such as concentration of the ENM within the product, daily usage of the product, fraction of the ENM removed during sewage treatment, and sludge application rates. Uncertainty is introduced into the model when data is not available for some of the necessary parameters. Uncertainty is also evaluated by allowing certain parameters (e.g. concentration of ENM within the product) to vary to calculate a range of PECs.

Blaser et al. (2008) modeled the emissions of silver (Ag) from biocidal products that held nano-silver. The model was designed to estimate the emissions of silver and analyze the mass flow as a result of emission, assess the fate and estimate the PECs of silver in a river system, estimate the PNECs through critical evaluation of available toxicity data for environmentally relevant forms of silver, and characterize the risk. Many simplifying assumptions such as neglecting emissions from production or solid waste, as well as the removal of marine environments from the system provide a simple model that may not encapsulate the characteristics of the broader life cycle of ENMs.

Mueller and Nowack (2008) present a model intended to address the quantities of engineered ENMs released into the environment from a life-cycle perspective. Using material flow analysis, three types of nanoparticles were studied: nano-silver, nano-titanium oxide, and carbon nanotubes. The model incorporated estimated worldwide production, particle release from products, and flow coefficients within the compartments selected for the model. The different life cycles of the three products generated varied results for the PECs. These generated PECs were then compared to the PNECs specific to each material in order to estimate potential risk.

Gottschalk et al. (2010a) developed a probabilistic material flow analysis (PMFA) to calculate distributions PECs and PNECs in a system comprised of 11 compartments. The paper used PMFA specifically to address the lack of data concerning environmental fate, exposure, emission, and transmission characteristics of ENMs. This stochastic approach allows the model to represent uncertainties based on estimated input parameters. The authors propose that the use of Monte Carlo simulations and Markov Chain Monte Carlo modeling is appropriate to estimate PECs when faced with limited of data.

4.2.4.2 Regulatory Multimedia Models

The six multimedia risk assessment models described in this section represent current, accepted approaches for multimedia modeling within the regulatory community. None of these models provides a comprehensive solution for estimating the fate of ENMs in the environment. Many of the associated sub-models do not account for key processes of particulate transport in the environment such as aggregation, attachment, settling, and porous media filtering. In addition, these traditional multimedia models are strongly reliant on chemical property estimation tools (e.g., QSARs) that were developed for chemicals other than ENMs (see **Section 2.3.10**). Some of the multimedia modeling frameworks are highly abstracted and only describe mass transfer between environmental compartments using simple mass transfer functions rather than mechanistic formulations that account explicitly for underlying processes. Such highly abstracted multimedia models may be useful for screening type evaluations of ENM transport; indeed, multimedia models specific to ENMs discussed in the previous section fall within this category. However, parameterization of such models generally will require knowledge (e.g., empirical data) that is currently unavailable for ENMs. Given these significant limitations, we have only provided brief summary descriptions of the traditional multimedia models described below.

FRAMES (Framework for Risk Analysis in Multimedia Environmental Systems and subsequent versions) and **MIMS** (the Multimedia Integrated Modeling System) are two multi-agency software frameworks regarded as the best available in United States for multimedia risk assessment. These two frameworks borrow concepts and codes from other frameworks, such as STELLA and DIAS. The most notable use of FRAMES is the integration of 17 scientific models in the 3MRA model to accomplish multimedia, multi-pathway, and multi-receptor risk assessment. MIMS is an object-oriented framework, especially suitable for models with different spatial and temporal scales. Its conceptual design supports interchanging models and data sets (and modeling of physical, chemical, biological, and human systems), cross-platform portability to support off-the-shelf models and distributed computing. MIMS differs from FRAMES in that it provides mechanisms to allow feedbacks between models (i.e., dynamically coupled system).

The **3MRA** Modeling System is a suite of 17 environmental risk assessment modules originally designed to support the Hazardous Waste Identification Rule (HWIR). It uses FRAMES to allow integration of these varied modules and data. This model has been peer-reviewed by EPA’s Science Advisory Board (SAB) and is currently supported by ongoing activities at ORD to develop automated systems to populate the extensive databases required to run simulations.

TRIM (Total Risk Integrated Methodology) is an elaborate collection of multiple models (e.g., fugacity-based models, simple air quality models, human exposure models) developed to perform deterministic multimedia health and ecological risk assessments for hazardous air pollutants. It uses the MIMS framework for integration of the risk assessment process. TRIM provides risk metrics tables that can be used to further analyze, interpret, and visualize the results. (http://www.epa.gov/ttn/fera/trim_gen.html)

The **RESRAD (Residual Radioactivity Models)** family of codes is a comprehensive set of components that allow probabilistic multimedia risk assessment that are fully interoperable. The codes support multimedia modeling and provide capabilities for sensitivity and uncertainty analysis. RESRAD uses an OpenLink software framework for integration of environmental risk analysis and management. In addition, the technical support for RESRAD is extremely good. RESRAD uses as low as reasonably achievable (ALARA) analysis or a cost-benefit analysis that can help in the cleanup decision-making process. The code is supported by Argonne National Labs and frequently updated to enhance functionality; for example, recent updates include non-radioactive chemicals. (http://web.ead.anl.gov/resrad/home2/)

CalTOX (California Total Exposure Model for Hazardous Waste Sites) is an Excel-based fugacity model for multimedia risk assessment. Due to the simplicity of the model, its results have been incorporated into life-cycle assessment models (e.g., TRACI). The CalTOX model has been used primarily for the assessment of contaminated soils as the primary source of contamination; however, it has been adapted for multiple purposes, including the support of risk ranking schemes and life cycle assessments. The California Exposure Modeling Research Center at Berkeley has an active program that involves the continuing development of this model, in part, to run nested spatial scale calculations. (http://eetd.lbl.gov/ie/ERA/)

ARAMS (Army Risk Assessment Modeling System) is a multimedia risk assessment tool that specially addresses human health and the ecological risks associated with military relevant compounds (MRCs); however, it is applicable to any setting with contaminated sources or media. ARAMS uses FRAMES to integrate environmental models and databases. ARAMS considers temporal and spatial distribution of contaminants and lends itself to sensitivity and uncertainty analyses. ARAMS has functional links to multiple existing databases, such as the Integrated Risk Information System (IRIS), Health Effects Assessment Summary Table (HEAST), Environmental Residue Effects Database (ERED), and BSAF (http://el.erdc.usace.army.mil/arams/).

SADA (Spatial Analysis Decision Assistance) is unique among all the other risk assessment models presented because it is a decision analysis and support tool for risk assessment. SADA combines risk assessment with geographic information systems (GIS) and statistical analysis methods and sampling design to determine remedial design and cost-benefit analysis. Use of GIS provides the capability to explore data that is spatially distributed (http://www.tiem.utk.edu/~sada/index.shtml).

4.3 Alternative Approaches

It is apparent that risk assessment of ENMs will depend critically and sensitively on the issues and uncertainties surrounding their fate and transport in the environment (Wiesner et al., 2009). Because of this, we must address the question: *How can environmental behavior and risk be characterized for an emerging technology?* The logical first step might be to modify a conventional risk assessment to incorporate the environmental interactions and properties relevant to ENMs. However, traditional risk assessment modeling will introduce substantial and unquantifiable uncertainties due to paucity of data surrounding the persistence of environmentally relevant forms of ENMs. Thus, while these models may provide some insight into the complex systems surrounding ENM transport in the environment, they offer limited guidance as to the actual potential for adverse health and environmental effects. This creates a need to develop models and approaches that can explicitly address the uncertainties surrounding these complexities and behaviors of ENMs in the environment, and provide meaningful information to risk managers. Therefore, we must rethink the existing assessment paradigms with respect to the nature of ENMs and their transformations, biological interactions, and environmental transport so that effective risk management can be developed for ENMs.

Other authors have supported this position (Linkov et al., 2009a). For example, Grieger et al. (2009) argue that although conventional risk assessments are needed for responsible development, the process may take decades, leaving decision makers with little support in the near term. Given the immediate demands placed on decision makers, we must design more adaptive risk governance frameworks and alternative methods to support the characterization of potential risks associated with ENMs released into the environment (Hansen, 2009). Lowry and Casman (2009) also stress the need for developing new frameworks to describe the potential risks of ENMs in the environment. They suggest integration of laboratory results into risk analytic frameworks such that preliminary risk analyses can prioritize and identify the most relevant data gaps needed to aid in traditional risk assessment. Thus, with the current limitations of traditional risk assessment and the future impact on every aspect of our lives and society that nanotechnology is expected to have, this state-of-the-science review has incorporated alternate approaches to more traditional fate and transport models including[5]:

- Adaptive management and evaluation frameworks
- MCDA
- Bayesian approaches.

The above approaches can be used for relatively near-term decision making for exposure to ENMs and will be discussed in the rest of this section. **Appendix B** provides more detailed reviews of each of these approaches. **Table 4-1** summarizes advantages and limitations of each of these alternative approaches.

Table 4-1. Summary Evaluation of Alternative Approaches to ENM Risk Evaluation

Alternative Approach	Advantages	Limitations
Adaptive Management and Evaluation Frameworks	• flexible and adaptable because of the acceptance of available data • explores atypical pathways of exposure	• limited quantitative data • lacks thorough testing and validation

[5] Two additional alternative approaches were identified in the search process for this report: Precautionary matrices (PM) and Value of Information (VoI). PM is a simple scoring tool designed for use in early assessments of the potential exposure risk of a substance to human health and the environment (Höck et al., 2008). The associated safety matrix incorporates information about potential harmful effects, product life cycle, chemical properties, and potential exposure routes in order to gain a general understanding of the risks that may arise from these substances. The designers stress that while this tool cannot replace traditional risk assessments, these matrices can be used to prioritize research needs for emerging technologies. Given the simplicity of the approach and the relatively narrow applicability of the technique, we have not provided additional review information for PM. VoI is intended to quantify the improvement in expected value from obtaining new information before making a decision and can reveal methods to reduce risk or increase potential value. While VoI may be a valuable tool for risk management, its potential application for evaluating ENM risk has yet to be documented. Therefore, the approach has not been reviewed in this report.

Multicriteria Decision Analysis	• balances societal benefits against unintended side effects and risks • combines multiple lines of evidence to estimate the toxicity, risk, or exposure to ENMs given limited information on physical and chemical properties • scientifically sound decision analytical framework • ranks or groups all the alternatives through a structured process rather than suggesting a single replacement	• does not predict environmental fate • interpretation of MCDA is subject to parameter definitions defined by the user • outcomes may depend on the decision maker which can be influenced by personal goals and preferences
Bayesian Networks	• generally robust to imperfect knowledge • easily updated/modified as new scientifically relevant information becomes available • provides optimal decisions based on the parameters assigned to the model	• some networks can be too large and complex for current Bayesian algorithms

4.3.1 Adaptive Management and Evaluation Frameworks

An adaptive evaluation framework, which is a form of adaptive management, is an alternative method that can be used to resolve challenges in modeling ENMs. Adaptive management is an atypical environmental management method in which the process involves: (1) Setting goals and management objectives; (2) development of a model of the system being managed; (3) development of a range of management choices; (4) monitoring and evaluating outcomes of management decisions; and (5) development of a mechanism in which new information can be incorporated into the system for future decisions (learning attribute). Along with this process, adaptive management allows for, and encourages, revisiting and revising goals and objectives of the project as well as a collaborative structure for stakeholder participation and learning *(Linkov et. al, 2006).* Adaptive management can be divided into two approaches: passive and active. Both follow the first three steps of the adaptive management process however passive management studies only one alternative experiment at a time, while active management implements multiple alternative strategies and examines the outcomes.

Following the above structure, adaptive evaluation frameworks can be used to circumvent the lack of data needed for the traditional risk assessment of ENMs by identifying many exposure potentials based on criteria typically not included in the risk assessment paradigm. Possible added avenues of evaluation include the location of the ENM within a product (Hansen et al., 2007), the product life cycle and potential release points, and anticipated volumes of production (Metcalfe et al., 2009). Adaptive evaluation frameworks typically unite these parameters with more common evaluation parameters such as basic physical and chemical information available for the ENM.

It is important to note that because each model approach relies on differing parameters, there are multiple techniques in which these types of specific frameworks can be developed. However, most frameworks use a conceptual guideline in the early development of the framework to map potential pathways of exposure. These pathways can be as simple or complex as the developer chooses. For instance, the categorization framework presented by Hansen et al. (2008) considers only consumer exposure to products containing ENMs, thus neglecting possible exposure from many environmental factors. However, a more extensive example of a conceptual framework for potential exposure can be shown in **Figure 4-1**, which is the exposure pathway conceptualized by the SMARTEN (Metcalfe et al., 2009) technique for adaptive frameworks. This framework utilizes information from the ENM manufacture as well as generalized environmental processes and exposure pathways to make predictions about the environmental fate and effects of ENMs.

Once pathways are identified, adaptive management requires alternative solutions be explored in order to produce lower risk exposure potentials. The decision maker takes a decision which is then interpreted as a hypothesis that needs to be tested and validated. Validation could involve monitoring exposure levels such as environmental surveillance (Metcalfe et al., 2009) or evaluating potential exposures due to the location and concentration levels of ENMs within the product (Hansen et al., 2008). The findings are evaluated to determine if the hypothesis is to be confirmed or rejected. If rejected, a new hypothesis is generated and the process starts again. Therefore, adaptive evaluation frameworks view the management of a risk as a process consisting of many small decisions rather than a single decision (Hansen, 2009).

Because technologies are evolving that constantly generate new safety and health information, adaptive evaluation frameworks must be able to accommodate new data so that the most accurate risk assessment can be performed on emerging ENMs. This methodology allows risk assessors to be more proactive in evaluating all aspects of the life cycle of an ENM, thus aiding in decisions to produce lower risk ENM products.

Some of the emerging adaptive evaluation frameworks are: (a) Categorization frameworks (Hansen et al., 2007); and (b) SMARTEN (Metcalfe et al., 2009), which reports a governance framework for adaptive evaluation frameworks. Hansen et al. (2007) will be evaluated in detail in **Appendix B** using the guidelines from **Section 4.1**.

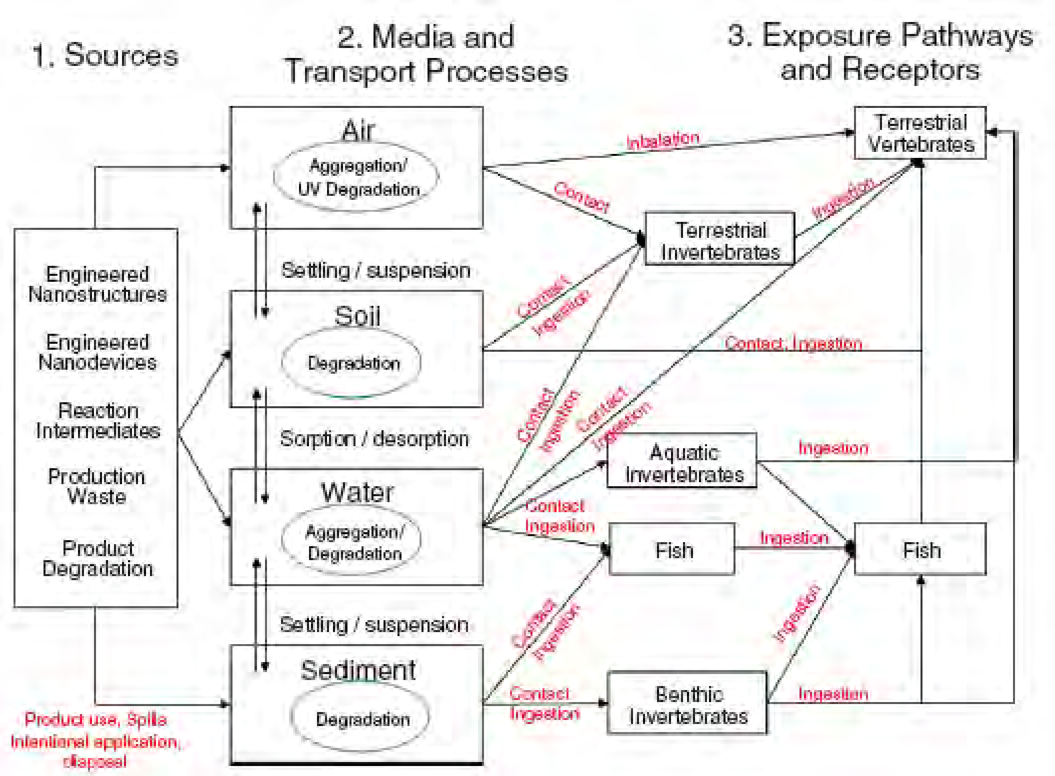

Figure 4-1. Conceptual exposure pathway utilized by the SMARTEN model.

4.3.2 Multi-Criteria Decision Analysis (MCDA)

This section presents a basic overview of MCDA techniques, including characteristics shared by different approaches. Within MCDA, almost all methodologies share similar steps of organization and decision matrix construction, but each methodology synthesizes information differently (Yoe, 2002; Figueira et al., 2005; Belton and Stewart, 2002). Different methods require diverse types of value information and follow various optimization algorithms. Some techniques rank options, some identify a single optimal alternative, some provide an incomplete ranking, and others differentiate between acceptable and unacceptable alternatives.

The MCDA methods are classified into two general categories of elementary methods and multi-objective methods that are considered more sophisticated and briefly discussed in the following.

4.3.2.1 Elementary Methods

Elementary MCDA methods (e.g., maximum method, conjunctive method, lexicographic method, and TOPSIS method) can be used to reduce complex problems to a singular basis for selection of a preferred alternative. However, these methods do not necessarily weight the relative importance of criteria and combine the criteria to produce an aggregate score for each alternative. While elementary approaches are simple and can, in most cases, be executed without the help of computer software, these methods are best suited for single-decision maker problems with few alternatives and criteria, a condition that is rarely characteristic of environmental projects.

In the maximum method, each alternative is scored based on the performance of its weakest attribute. The analogous maximax method scores each alternative based on the performance of its strongest attribute. Comparison of the alternatives requires that all attributes be scored on comparable scales.

The conjunctive method is designed to screen alternatives based on whether they exceed minimum performance thresholds for all criteria. One useful application of the conjunctive approach is to decrease a large number of alternatives to allow more detailed evaluation of a subset. The conjunctive method does not require attributes to be scored on a common scale, thereby limiting the effort needed for the analysis. In the analogous disjunctive method, alternatives pass the screening test if they exceed the minimum performance threshold for at least one attribute (as opposed to all attributes in the conjunctive method).

In the lexicographic method, the criteria are ordered in terms of importance. The alternative with the best performance is the alternative with the strongest performance for the most important criterion. If multiple alternatives are tied with respect to the most important criterion, these alternatives are compared for the next criterion, and so on, until the highest performing alternative is selected.

In the TOPSIS method (technique for order preference by similarity to ideal solution), the selected alternative should be as close to the ideal as possible and as far from the negative ideal as possible. The ideal is defined as a hypothetical alternative with the highest individual criteria scores. The negative ideal is the combination of minimum scores.

4.3.2.2 Multi-objective Methods

Some of the main multi-objective decision analysis methods include Multi-Attribute Utility Theory (MAUT), Multi-Attribute Value Theory (MAVT), Analytical Hierarchy Process (AHP), and outranking. Table 4-1 summarizes important elements, strengths and weaknesses of these methods (Linkov et al., 2007). The first three methods are more complex methods that use optimization algorithms, whereas outranking uses a dominance approach. The optimization approaches employ numerical scores to communicate the merit of each option on a single scale. Scores are developed from the performance of alternatives with respect to individual criteria and then aggregated into an overall score. Individual scores may be simply summed or averaged, or a weighting mechanism can be used to favor some criteria more heavily than others. The goal of MAUT is to find a simple expression for the net benefits of a decision. Through the use of utility or value functions, MAUT transforms diverse criteria into one common scale of utility or value. MAUT relies on the assumptions that the decision maker is rational (preferring more utility to less utility, for example), that the decision maker has perfect knowledge, and that the decision maker is consistent in his judgments. The goal of decision makers in this process is to maximize utility or value. Because poor scores on criteria can be compensated for by high scores on other criteria, MAUT is part of a group of MCDA techniques known as compensatory methods.

MAVT refers to decision analysis without formal uncertainty analysis, while MAUT refers to methodologies that formally account for uncertainty. In the literature, MAVT is typically treated as a subset of MAUT, and the more general term (MAUT) is more commonly used.

Similar to MAUT, AHP (Saaty, 1994) aggregates various facets of the decision problem using a single optimization function known as the objective function. The goal of AHP is to select the alternative that results in the greatest value of the objective function. Like MAUT, AHP is a compensatory optimization approach. However, AHP uses a quantitative comparison method that is based on pair-wise comparisons of decision criteria rather than utility and weighting functions. All individual criteria must be paired against all others and the results compiled in matrix form. For example, in examining the choices in the selection of an ENM, AHP would require the decision maker to answer questions such as, ‘‘With respect to the selection of an ENM, which is more important, its economic impacts or its environmental impacts?’’ The user uses a numerical scale to compare the choices and AHP moves systematically through all pair-wise comparisons of criteria and alternatives. AHP thus relies on the supposition that humans are more capable of making relative judgments than absolute judgments. Consequently, the rationality assumption in AHP is more relaxed than in MAUT.

Unlike MAUT and AHP, outranking is based on the principle that one alternative may have a degree of dominance over another (ODPM, 2004). Dominance occurs when one option performs better than another on at least one criterion and no worse than the other on all criteria (ODPM, 2004). However, outranking techniques do not presuppose that a single best alternative can be identified. Outranking models compare the performance of two (or more) alternatives at a time, initially in terms of each criterion, to identify the extent to which a preference for one over the other can be asserted. Outranking techniques then aggregate the preference information across all relevant criteria and seek to establish the strength of evidence favoring selection of one alternative over another. For example, an outranking technique may entail favoring the alternative that performs the best on the greatest number of criteria. Thus, outranking techniques allow inferior performance on some criteria to be compensated for by superior performance on others. They do not necessarily, however, take into account the magnitude of relative underperformance in a criterion versus the magnitude of over-performance in another criterion. Therefore, outranking models are known as partially compensatory. Outranking techniques are most appropriate when criteria metrics are not easily aggregated, measurement scales vary over wide ranges, and units are incommensurate or incomparable.

4.3.2.3 Recent Reports and Models

There are many different forms of MCDA available for use, such as the stochastic multicriteria acceptability analysis (SMAA-TRI), AHP, and MAUT. Linkov et al. (2007) and Linkov et al. (2009b) explore some of these techniques and how they can be utilized in ENM decision making. These reports will be evaluated in detail in **Appendix B** using the guidelines from **Section 4.1**.

4.3.3 Bayesian Approaches

Bayesian Networks, or BayesNets, provide a framework for adaptable risk assessment that can account for various types of uncertainty and may be easily updated/modified as new scientifically relevant information becomes available. Much of this discussion is based upon work at CEINT directed by Dr. Mark Wiesner. Bayesian approaches are a major focus of their efforts to develop approaches for evaluating ENM behavior in the environment.

BayesNets are probabilistic networks. A network, or graph, provides a mathematical structure composed of nodes (vertices) and edges. Edges join pairs of vertices and represent a pairwise relationship between two nodes. Two nodes are said to be connected if a path of edges exists that can be followed from one vertex to the other. Graphs can be undirected or directed. In a directed graph, relationships move in one direction, whereby one vertex influences another but not vice-versa. In an undirected graph, influence can occur in either direction. A network is probabilistic if probabilities (also known as weights) are assigned to the edges. The weights represent the likelihood of a relationship occurring between nodes.

Bayesian networks are based on directed, acyclic graphs representing a set of random variables (nodes) and their conditional dependences (edges). For the modeling of ENM exposure to the environment, a Bayesian network may represent the probabilistic relationship between environmental media and the amount of ENM present in the system. Given an amount of ENM produced, the network can be used to estimate the amount of ENM in specific environmental media based on the likelihoods of material flow through the network.

The development of a Bayesian network offers two significant advantages: (1) because a Bayesian network only connects nodes that are probabilistically related, an enormous computational saving can result; and (2) Bayesian networks are extremely adaptable. Traditionally, probabilistic models could lead to excessive numbers of potential states to be solved, which could require impractical computational efforts. Bayesian networks offer a solution to the computational challenges by limiting the possible combinations of states based on probabilistic relationships. The adaptability of Bayesian networks lies in the fact that networks can be expanded or modified as scientifically relevant information emerges.

Some have refrained from using BayesNets due to the belief that they will only work well if the probabilities upon which they are based are exact. In actuality, approximate probabilities, even those based on professional judgment, can provide very useful results. In other words, BayesNets are generally robust to imperfect knowledge. Thus, the combination of several strands of imperfect knowledge can still allow surprisingly strong conclusions.

Figure 4-2 displays a network developed by CEINT designed to predict environmental exposure to ENMs. Network nodes represent ENM mass residing within the system, and edges represent material flows through the system. The nodes may be either: (1) a source of ENM; or (2) an environmental compartment in the system where ENMs may reside. Sources of ENMs may include: initial production sources of raw ENMs (S); intermediate products containing ENMs (I); and final products containing ENMs (P). For the CEINT model, the environmental compartments included are atmosphere, wastewater treatment plant (WWTP), storage, landfill, effluent, sludge, natural waters, and agricultural land. The directed edges indicate the flow of ENM from one compartment (node) to another. In the case of edges from products to environmental compartment, this represents the leakage (i.e., release of ENMs into the environment). Leakage can be aggregated over environmental compartments or over specific stages of the value chain

(NM production, use, and transport as products are produced). For example, the directed edge from S into the atmosphere compartment represents the potential loss of ENM from the raw ENMs used for production into the immediate atmosphere. A probabilistic relationship for each flow path (edge) must be defined for this to be a Bayesian network. The probabilistic relationship assigned to each edge designates the fraction of ENM that moves from one node to the next. A framework for describing ENM production and incorporation into products as well as leakage to the environment can now be explored.

From this generalization (Figure 4-2), flows in this system can be characterized. Conceptually, the description of all flows within this network represents a very high demand for information on trends in commercialization, product use, product degradability, and ENM transformation and transport. However, the framework provides the ability to aggregate across the value chain or across receiving compartments such as wastewater, thereby reducing the number of unknowns at the cost of loss of detail. For example, the amount of ENM entering the wastewater compartment can be expressed as the product of the ENM source term and the sum of products of coefficients representing all pertinent intermediate flows. This aggregation yields a single coefficient that captures ENM production and use profiles relevant to the wastewater compartment. Though the value of this coefficient may not be known initially, it may be estimated from measurements of the quantities of ENMs in wastewater or from commercial projections and assumptions of use of these products. Moreover, assumptions regarding the amount of ENMs entering wastewater are made explicit through the specification of the coefficient and can be examined in what-if scenarios. In this fashion the concentration of NPs that make their way into in wastewater sludge and can be estimated by the above network using equations that will be available upon completion of the work. Differences in production/usage profiles and the physical-chemical characteristics of the ENMs determine their environmental fate with respect to wastewater treatment residuals (sludge and treated water). Similar conceptual equations can be developed for ENMs entering surface waters, landfills, and the atmosphere. Associated production/usage profiles and transfer functions will be generated through the CEINT research.

The broad variety of materials made into NPs (e.g. metals, oxides, or carbon-based), the technical difficulties associated with measuring NPs at low concentrations, and the added complexity of detecting particles in the complex media that constitute natural waters, soils, and air, present significant challenges to estimating potential exposures to ENMs. The Bayesian network approach for ENM exposure assessment described above requires quantitative relationships between the amounts of ENMs entering disposal and treatment systems and environmental compartments. Thus, transfer functions must be developed for each environmental compartment considering properties necessary for transport in the specified media.

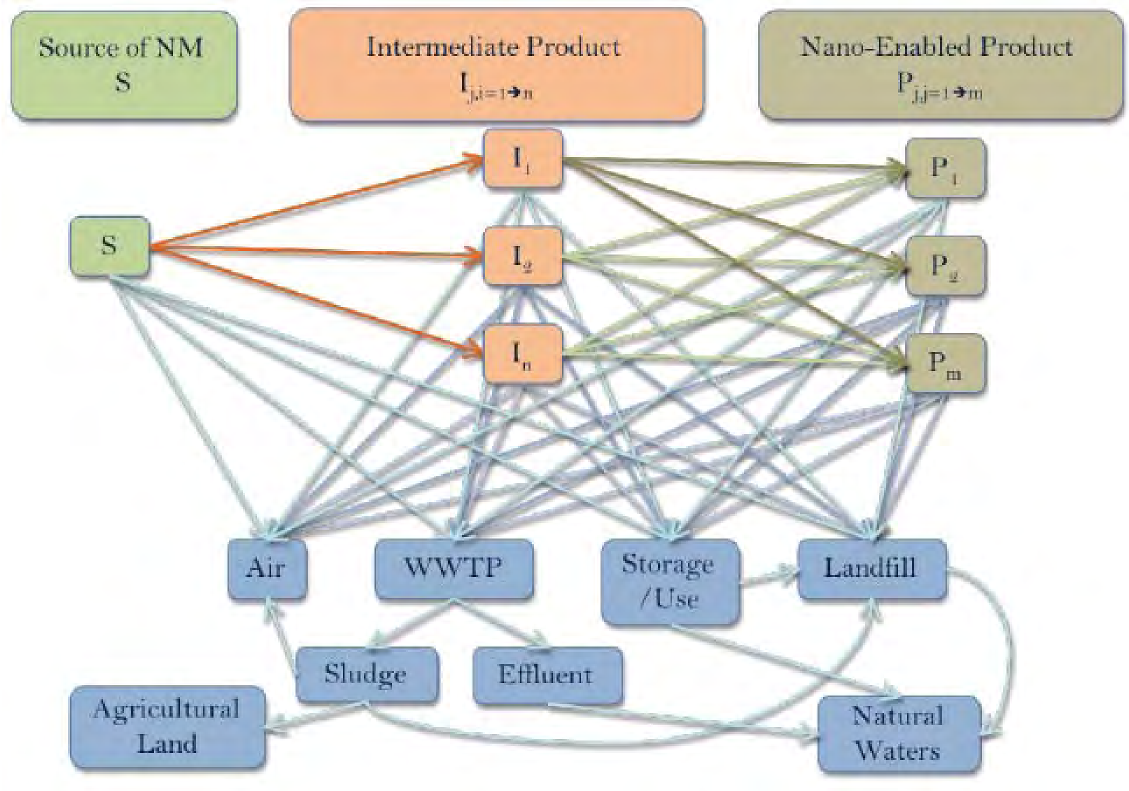

Figure 4-2. Conceptual network of ENM flows over value chain and into environmental compartments.

Chapter 5.0
Conclusions

In this section, conclusions are drawn from the state-of-the-science review of models and methods relevant to the exposure assessment of ENMs released into the environment. These conclusions are presented with respect to the five basic questions that this review was designed to answer, for convenience, repeated below.

1. What models and approaches have been used successfully to simulate nanomaterial behavior in environmental systems?
2. What models and approaches *cannot* be used to predict exposures to ENMs in ecosystems?
3. What models and approaches can be used in the near term, and what types of predictions can be supported by available models?
4. What techniques can be used to address uncertainties and support risk management decisions in the near term given obvious gaps in information?
5. What does the state-of-the-science suggest with respect to long-term research goals that can be undertaken to improve fate and transport modeling tools for ENMs?

The remainder of this section discusses each of these science questions with respect to results of the state-of-the-science for exposure modeling of ENMs in the environment.

What models and approaches have been used successfully to simulate nanomaterial behavior in environmental systems?

Fate and transport models that predict the behavior of ENMs in the environment must consider particulate transport behaviors, including processes of aggregation and disaggregation, attachment and detachment, settling and sedimentation, filtering and enhanced transport in porous media, as well as particulate diffusion (see **Section 2.3** for further discussion of these processes related to ENMs). We identified several models (see **Section 4**) that account for many of these particulate processes, including models developed specifically for ENMs, some established regulatory models, and models originally developed for other purposes (e.g., colloid transport models). However, even if models incorporate descriptions of key particulate-transport behaviors, there remain significant knowledge gaps for ENMs. Reliable parameterization of such models will not be possible until sufficient data (laboratory and field) are available. Therefore, the utility of these models to predict ENM concentrations in the environment in the near term is limited.

Several alternative approaches to traditional risk assessment that are rooted in risk management and decision analysis offer the ability to evaluate ENMs risks in the short term without necessarily requiring extensive data collection. Furthermore, these alternative approaches offer distinct advantages in terms of integrating different types of information (e.g., expert knowledge and scientific judgment) and account for uncertainty and incomplete knowledge. **Section 4.3** provided an introduction to several promising alternative approaches, including adaptive evaluation frameworks, MCDA, and Bayesian approaches. Although these alternative approaches may not be sufficiently robust to support prescriptive regulatory requirements in the near term (e.g., setting allowable concentration limits), they may provide information on *relative risks*, which can be useful in risk management. Risk ranking results could be used to prioritize research studies (i.e., characterize those ENMs with the greatest potential risk) as well as to prioritize regulatory initiatives such as voluntary agreements with industry to avoid potentially high risk practices.

What models and approaches cannot be used to predict exposures to ENMs in ecosystems?

Models that do not consider critical particulate-transport behaviors and associated properties show little promise for the evaluation of ENM transport. Many established regulatory models do not account for key ENM behaviors (see **Section 4**). In addition, many established fate and transport models are based on traditional equilibrium partitioning relationships. Existing estimates of partition coefficients (e.g., those based on QSARs) are generally invalid for materials at the nanoscale due primarily to the fact that ENMs exhibit properties of particles as well as chemicals (see **Section 2.3.10**). Furthermore, enhanced partitioning models will likely be required to predict ENM behaviors reliably (i.e., models that account for the distribution of mass between solid, aqueous, as well as particulate phases and potentially nonequilibrium, kinetic mass transfer).

It is important to recognize that environmental risk assessment often relies on low or moderate complexity models that describe detailed transport mechanisms using relatively simple model constructs (sometimes referred to as lumped parameter, conceptual models; see Box 4-1). Such approaches are necessary (and appropriate) to simulate the fate and transport of conventional chemicals, even though they are simplifications of natural systems that are variable and complex. However, the use of such models involves uncertainty, as emphasized in the silver book, and it is critical to characterize and, where possible, quantify the uncertainty in the risk estimates. It is as yet unknown whether such lumped-parameter formulations will be appropriate for simulating the behavior of ENMs in environmental systems or whether alternative modeling constructs will be required. Regardless, lumped parameter models must be grounded in empirical evidence in order to make reliable predictions (given their empirical or semi-empirical basis, they cannot make reliable predictions a priori). Therefore, even if the underlying model constructs ultimately are shown to be appropriate (i.e, model structural analysis), the current applicability of these models for predicting ENM behavior is significantly limited by a lack of knowledge and lack of available, empirical data to ensure reliable predictions.

What models and approaches can be used in the near term, and what types of predictions are currently supported?

The alternative approaches described in **Section 4.3** can be applied in the near term to evaluate risks associated with nanomaterials released to the environment. Some of these approaches result in a qualitative (or semi-quantitative) relative ranking of potential risks from specific ENMs. To the extent that these approaches produce quantitative results (e.g., predicted environmental concentrations), current gaps in our knowledge will create significant and possibly unquantifiable uncertainties. Nevertheless, the relative risk results should provide important insights for regulatory decision makers in the near term.

What techniques can be used to address the uncertainties and support risk management decisions in the near term given obvious gaps in information?

The alternative approaches described in **Section 4.3** provide promising methods for near term evaluation of ENM exposures. Several of these approaches address uncertainties explicitly. For example, the BayesNet approach is a probability-based approach that produces probability distributions for estimated exposures and effects. Some of the reviewed fate and transport models (**Section 4.2**) show promise for ENMs, and many of these models may be implemented using methods developed to represent variability and uncertainty (e.g., Monte Carlo analysis). However, the extensive data gaps associated with ENMs limit the utility of fate and transport models in the near term.

What does the state-of-the-science suggest with respect to long-term research goals that can be undertaken to improve fate and transport modeling tools for ENMs?

In concluding this state-of-the-science report, we offer the following to inform the development of an integrated research strategy for exposure modeling of ENMs:

- As emphasized in this report, there are significant data gaps in the understanding of nanomaterial behaviors in the environment. Naturally, research should continue to support the development of a basic understanding of the fundamental mechanisms controlling fate and transport. This research should include: (1) empirical studies (laboratory and field) to characterize ENM transport under a variety of natural conditions and to develop parameters in support of ENM modeling; (2) the field testing of existing models to develop insight into the magnitude of their current limitations; and (3) given the importance of the partitioning approach in multimedia modeling, new modeling approaches should be developed to replace or modify the partitioning approach used for conventional organic chemicals.
- The prevalent data gaps in characterizing ENMs will severely limit the ability to predict ENM transport using existing fate and transport models, even if these models account for key particulate-transport processes associated with ENMs. It may require years to develop sufficient knowledge and modeling expertise that support reliable predictions of the environmental behavior of ENMs. Given these challenges, alternative approaches (described in **Section 4.3**) can be used to support science-based risk management, explicitly acknowledging uncertainties in the estimation of exposures. Therefore, we recommend a parallel research track (along with fundamental fate and transport research) that promotes decision analytic and/or adaptive management approaches that, ultimately, can be linked to mechanistic fate and transport models/data under development.
- We recommend a state-of-the-science evaluation similar to the current report that is focused on non-organic ENMs, most notably metals. The focus of the current report was on organic-based ENMs, although many of the concepts discussed are more broadly applicable.
- Multiple references emphasized the lack of consistency in reporting (and measuring) ENM properties as well as ambiguity in nomenclature for this emerging field. In addition, the large number of ENMs and their highly variable properties and behaviors suggest that

different modeling and parameterization approaches will be required for different types of ENMs. Therefore, we suggest a model-based classification system for ENMs that captures differences and similarities in environmental behaviors and dependencies. Such a classification system would (at a minimum) need to consider the chemical composition of the base material (e.g., organic versus metal) as well as the composition of any surface modification to the ENM. Development of a standard ENM data model that links fate and transport modeling needs to basic research standards on ENM properties would provide a more integrated approach to environmental modeling of ENMs. Such a data model would support key input parameter requirements for fate and transport models—a core data set required for each class of ENM. This data model may in turn lead to characterization and reporting recommendations for ENM manufacturers, thereby providing much needed data for environmental fate and transport modeling and risk assessment.

Chapter 6.0
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Appendix A
Titles Pertaining to the Use of Exposure Models for Nanomaterials

(references highlighted in blue are reviewed in Appendix B)

Exposure Science and Model Evaluation					
Title	**First Author**	**Date**	**Source**	**Content**	**Number of References**
Meeting Report: Hazard Assessment for Nanoparticles—Report from an Interdisciplinary Workshop	Balbus, J.	2007	Meeting Report	Risk assessment	15
Towards a framework for life cycle thinking in the assessment of nanotechnology	Bauer, C.	2008	Article	Research	60
Understanding risk assessment of nanotechnology	Bell, T.	2007	Article	Risk assessment	44
Nanoparticles and the environment	Biswas, P.	2005	Article	Review	387
Where Does the Nano Go? End-of-Life Regulation of Nanotechnologies	Breggin, L.	2007	Report	Review	233
Nanoparticles: Their potential toxicity, waste and environmental management	Bystrzejewska-Piotrowska, G.	2009	Article	Review	104
Nano risk framework	Environmental Defense Fund	2007	Report	Risk assessment	70
The Appropriateness of Existing Methodologies to Assess the Potential Risks Associated with Engineered and Adventitious Products of Nanotechnologies	European Commission SCENIHR	2006	Report	Review, risk assessment	approx. 220
Redefining risk research priorities for nanomaterials	Grieger	2010	Article	Review, risk assessment	71
Research Strategies for Safety Evaluation of Nanomaterials, Part II: Toxicological and Safety Evaluation of Nanomaterials, Current Challenges and Data Needs	Holsapple, M.	2005	Article	Framework, review	36
Uncertainty and precaution in environmental management	Krayer von Krauss, M.	2005	Article	Model development	40

A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks	Lam, C.	2006	Article	Review	105
Nano-risk and macro-uncertainty: Using probability networks to model the environmental implications of nanotechnology	Money, E.	2009	Abstract	Model development	3
Do Nanoparticles Present Ecotoxicological Risks for the Health of the Aquatic Environment?	Moore, M.	2006	Article	Review, risk assessment	101
Exposure Modeling of Engineered Nanoparticles in the Environment	Mueller, N.	2008	Article	Review, model development	34
Models in Environmental Regulatory Decision Making	NRC, Committee on Models in the Regulatory Decision Process	2007	Book	Model development, review	approx. 150
Science and Decisions: Advancing Risk Assessment	NRC, Committee on Improving Risk Analysis Approaches used by the U.S. EPA	2009	Book	Risk assessment	approx. 150
Occurrence, Behavior and Effects of Nanoparticles in the Environment	Nowack, B.	2007	Article	Review	255
Ecological uptake and depuration of carbon nanotubes by *Lumbriculus variegates*	Petersen E.	2008	Article	Research	34
Safety Assessment for Nanotechnology and Nanomedicine: Concepts of Nanotoxicology	Oberdörster G.	2010	Article	Review	71
Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy	Oberdörster, G.	2005a	Article	Risk assessment	183
Nanotoxicology: An emerging discipline evolving from studies of ultrafine particles	Oberdörster G.	2005b	Article	Review	93
Risk Governance in a Complex World	Renn, O.	2008	Book	Research, risk assessment	n/a
In vivo Biomodification of Lipid-Coated Carbon Nanotubes by Daphnia magna	Roberts, A.	2007	Article	Research	16

International Risk Governance Council Policy Brief: Nanotechnology Risk Governance: Recommendations for a Global, Coordinated Approach to the Governance of Potential Risks	Roco, M.	2007	Presentation	Risk governance	0
Exposure to carbon nanotube material: assessment of nanotube cytotoxicity using human keratinocyte cells	Shvedova, A.	2003	Article	Research	53
Research strategies for safety evaluation of nanomaterials, Part I: Evaluating the human health implications of exposure to nanoscale materials	Thomas, K.	2005	Article	Review	16
Research strategies for safety evaluation of nanomaterials, Part VII	Thomas, T.	2006	Article	Review	12
Considerations for environmental fate and ecotoxicity testing to support environmental risk assessment from engineered nanoparticles	Tiede, K.	2009	Article	Review	85
Research strategies for safety evaluation of nanomaterials, Part IV: risk assessment of nanoparticles	Tsuji, J.	2006	Article	Review, risk assessment	61
Nanotechnology White Paper	US EPA	2007	Report	Framework	182
A Conceptual Framework for U.S. EPA's National Exposure Research Laboratory	US EPA	2009a	Report	Framework	13
Hexahydro-1,3,5-trinitro-1,3,5-triazine Transformation by Biologically Reduced Ferrihydrite: Evolution of Fe Mineralogy, Surface Area, and Reaction Rate	Williams, A.	2005	Article	Research	50
Recent Reports and Compendia					
Title	**First Author**	**Date**	**Source**	**Content**	**Number of References**
Ecotoxicity of engineered nanoparticles to aquatic invertebrates: a brief review and recommendations for future toxicity testing	Baun, A.	2008	Article	Review	39
A Guide for the Safe Handling of Engineered and Fabricated Nanomaterials	Greaves-Holmes, W.	2009	Article	Review	31
The known unknowns of nanomaterials: Describing and characterizing uncertainty within environmental, health and safety risks	Grieger, K.	2009	Article	Review	64

Factors Influencing the Partitioning and Toxicity of Nanotubes in the Aquatic Environment	Kennedy, A,	2008	Article	Research	39
EMERGNANO: A review of completed and near completed environment, health and safety research on nanomaterials and nanotechnology	IOM, for U.K. DEFRA	2009	Report	Review	71
Nanotechnology: A Research Strategy for Addressing Risk	Maynard, A.	2006	Report	Review, risk assessment	44
Approaches to Safe Nanotechnology: Managing the Health and Safety Concerns Associated with Engineered Nanomaterials	NIOSH	2009	Report	Review, risk assessment	approx. 180
Environmental fate and ecotoxicity of engineered nanoparticles	Norwegian Pollution Control Authority	2008	Report	Review	125
Engineered Nanoparticles: Review of Health and Environmental Safety (ENRHES)	Stone, V. (project coordinator) of Edinburgh Napier University	2009	Report	Review, risk assessment	approx. 90
Moving toward exposure and risk evaluation of nanomaterials: challenges and future directions	Thomas, T.	2009	Article	Review, risk assessment	25
A scoping study to identify hazard data needs for addressing the risks presented by nanoparticles and nanotubes	Tran, C.	2005	Report	Review, risk assessment	264
Characterising the potential risks posed by engineered nanoparticles	DEFRA	2005	Report	Review, risk assessment	50
Sampling and Analysis of Nanomaterials in the Environment: A State-of-the-Science Review. Final Report	US EPA [Varner, K.]	2008	Report	Review, risk assessment	39
Nanomaterial Research Strategy	US EPA	2009b	Report	Framework, review, risk assessment	43
Decreasing Uncertainties in Assessing Environmental Exposure, Risk, and Ecological Implications of Nanomaterials	Wiesner, M.	2009	Article	Review	62

Models that Simulate Particle, Aerosol, Polymer, and Colloid Behavior					
Title	**First Author**	**Date**	**Source**	**Content**	**Number of References**
Two-Dimensional Modeling of Contaminant Transport in Porous Media in the Presence of Colloids	Bekhit, H.	2005	Article	Model development	49
Exchange of TiO 2 Nanoparticles between Streams and Streambeds	Boncagni, N.	2009	Article	Research	32
A Stochastic Model for Colloid Transport and Deposition	Bradford, S.	2007	Article	Model development	65
Aggregation and deposition characteristics of fullerene nanoparticles in aqueous systems	Brant, J.	2005	Article	Research	24
Application of an empirical transport model to simulate retention of nanocrystalline titanium dioxide in sand columns	Choy, C.	2008	Article	Research	21
Modeling colloid transport for performance assessment	Contardi, J.	2001	Article	Model development	18
Modeling colloid transport in unsaturated porous media and validation with laboratory column data	Corapcioglu, M.	1996	Article	Model development, research	18
Simulation of the Subsurface Mobility of Carbon Nanoparticles at the Field Scale	Cullen, E.	2010	Article	Model development, research	51
Transport and retention of colloidal aggregates of C60 in porous media: Effects of organic macromolecules, ionic composition, and preparation method	Espinasse, B.	2007	Article	Research	31
Comparative toxicity of nanoparticulate ZnO, bulk ZnO and ZnCl2 to a freshwater microalga (Pseudokirchneriella subcapitata): The importance of particle solubility	Franklin, N.	2007	Article	Research	38
Dispersion and solubilization of carbon nanotubes	Fu, K.	2003	Article	Review	88
A review of non-DLVO interactions in environmental colloidal systems	Grasso, D.	2002	Article	Model development, review	approx. 130
Deposition and re-entrainment dynamics of microbes and non-biological colloids during non-perturbed transport in porous media in the presence of an energy barrier to deposition	Johnson, W.	2007	Article	Research, review	154

Experimental study and mathematical model of nanoparticle transport in porous media	Ju, B.	2009	Article	Model development, research	20
Two Dimensional Transport Characteristics of Surface Stabilized Zero-valent Iron Nanoparticles in Porous Media	Kanel, S.	2008	Article	Research	30
Critical Review: Nanomaterials in the Environment: Behavior, Fate, Bioavailability, and Effects. Environmental Toxicology and Chemistry	Klaine, S.	2008	Article	Review	249
Adsorption of Cadmium (II) from aqueous solution by surface oxidized carbon nanotubes	Li, Y.	2003	Article	Model development, research	23
Investigation of the Transport and Deposition of Fullerene (C60) Nanoparticles in Quartz Sands under Varying Flow Conditions	Li, Y.	2008	Article	Model development, research	34
Mobility of Multiwalled Carbon Nanotubes in Porous Media	Liu, X.	2009	Article	Model development, research	36
Stochastic probability modelling to predict the environmental stability of nanoparticles in aqueous suspension	Mackay, C.	2006	Article	Model development	11
Preliminary 3-D site-scale studies of radioactive colloid transport in the unsaturated zone at Yucca Mountain, Nevada	Moridis, G.	2003	Article	Research	52
EOS9nT: a TOUGH2 Module for the Simulation of Flow and Solute/Colloid Transport	Moridis, G.	1999	Report	Model development, research	46
A physiochemical model for colloid exchange between a stream and a sand streambed with bed forms	Packman, A.	2000	Article	Model development	40
Protein interaction with hydrated C(60) fullerene in aqueous solutions	Rozhkov, S.	2003	Article	Research	16
Colloid Mobilization and Transport in Contaminant Plumes: Field Experiments, Laboratory Experiments, and Modeling	Ryan, J.	1999	Report	Model development, research	111
Colloid-associated contaminant transport in porous media: 1. Experimental studies	Sen, T.	2002a	Article	Research	28
Colloid-associated contaminant transport in porous media: 2. Mathematical modeling	Sen, T.	2002b	Article	Model development	21
Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media	Sen, T.	2006	Article	Review	215

Toxicity of single-walled carbon nanotubes to rainbow trout (*Oncorhynchus mykiss*): Respiratory toxicity, organ pathologies, and other physiological effects	Smith, C.	2007	Article	Research	44
A novel two-dimensional model for colloid transport in physically and geochemically heterogeneous porous media	Sun, N.	2001	Article	Model development	52
Life-cycle effects of single-walled carbon nanotubes (SWNTs) on an estuarine meiobenthic copepod	Templeton, R.	2006	Article	Research	40
MNM1D: A Numerical Code for Colloid Transport in Porous Media. Implementation and Validation	Tosco, T.	2009	Article	Model development, research	31
Transport of reactive colloids and contaminants in groundwater: effect of nonlinear kinetic interactions	van de Weerd, H.	1998	Article	Research	27
Potential for the formation and migration of colloidal material from a near-surface waste disposal site	Vilks, P.	1998	Article	Research	30
Transport and Retention of Nanoscale C 60 Aggregates in Water-Saturated Porous Media	Wang, Y.	2008	Article	Research	35
Photocatalytic decomposition of seawater-soluble crude-oil fractions using high surface area colloid nanoparticles of TiO_2	Ziolli, R.	2002	Article	Research	19

Multimedia Models Currently Used in Fate and Transport Simulation					
Title	**First Author**	**Date**	**Source**	**Content**	**Number of References**
Estimation of cumulative aquatic exposure and risk due to silver: contribution of nanofunctionalized plastics and textiles.	Blaser, S.	2008	Article	Model development, research	64
Current and Predicted Environmental Exposure to Engineered Nanoparticles	Boxall, A.	2007a	Report	Research	112
Engineered nanomaterials in soils and water: how do they behave and could they pose a risk to human health?	Boxall, A.	2007b	Article	Review, risk assessment	50
Probablilistic material flow modeling for assessing the environmental exposure to compound: Methodology and an application to engineered nano-TiO2 particles	Gottschalk, F.	2010a	Article	Model development	55
Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis	Gottschalk, F.	2010b	Article	Model development	71
Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments	Koelmans, A.	2009	Article	Research	57
Alternative Approaches and Models					
Title	**First Author**	**Date**	**Source**	**Content**	**Number of References**
Categorization framework to aid exposure assessment of nanomaterials in consumer products	Hansen, S.	2008	Article	Framework, research	12
A toxicologic review of quantum dots: Toxicity depends on physicochemical and environmental factors	Hardman, R.	2006	Article	Review	48
Guidelines on the Precautionary Matrix for Synthetic Nanomaterials	Höck, J.	2008	Paper	Model development	n/a
Classifying Nanomaterial Risks Using Multi-Criteria Decision Analysis	Linkov, I.	2009b	Book	Model development, risk assessment	37
Multi-criteria decision analysis and environmental risk assessment for nanomaterials	Linkov, I.	2007	Article	Model development	25

Use of multi-criteria decision analysis tools to facilitate weight-of-evidence evaluation in nanotechnology risk assessment	Linkov, I.	2006	Conference	Model development, review	n/a
From Comparative Risk Assessment to Multi-Criteria Decision Analysis and Adaptive Management: Recent Developments and Applications.	Linkov, I.	2006	Article	Model development, review	81
SMARTEN: strategic management and assessment of risks and toxicity of engineered nanomaterials	Metcalfe, C.	2009	Book	Model development, risk assessment	44
Development of a preliminary framework for informing the risk analysis and risk management of nanoparticles	Morgan, K.	2005	Article	Review, risk assessment	21
Is anything out there? What life cycle perspectives of nano-products can tell us about nanoparticles in the environment	Nowack, B.	2008	Article	Review	1
DLTR Multi-Criteria Decision Analysis Manual	Office of the Deputy Prime Minister (ODPM), UK	2004	Report	Model development, review	approx. 50
Concept of assessing nanoparticle hazards considering nanoparticle dosemetric and chemical/biological response metrics	Rushton, E.	2010	Article	Research	41
Colloid-Facilitated Solute Transport in Variably Saturated Porous Media: Numerical Model and Experimental Verification [HYDRUS]	Šimůnek, J.	2006	Article	Model development	69
Precautionary Principle Analyzed	Treder, M.	2003	Article	Review	9
Trade-Off Analysis Planning and Procedures Guidebook	Yoe, C.	2002	Report	Model development, review	>150

Appendix B
Exposure Model/Method Summaries for NMs in the Environment

List of Reviewed Models and Methods

Appendix B provides model reviews that are structured according to the categories discussed in **Section 4.1**. We have provided reviews for models that have been developed for and/or applied to ENMs as well as other models that have potential applicability (in their present form) for the evaluation of ENM transport in the environment. Some review categories were not applicable to all models. In those cases, we note that the categories/questions are not applicable to the model. **Table B-1** provides a summary categorical overview of the models reviewed within this Appendix.

Table B-1. Summary of Models Reviewed

Model Reference	Overview		Model Type		Peer Review		Availability and Usability			Page Reference
	Natural	Engineered	Deterministic (D) or Probabilistic (P)	Process-based (P) or Statistical (S)	Journal Article	External Peer Review	User-interface	Use of proprietary algorithms	Source code available	
Surface Water Models										
Mackay et al. (2006)		X	P	S						B-4
Koelmans et al. (2009)	X	X	D	P	X					B-7
Packman et al. (2000)		X	D	P	X					B-10
Subsurface Models										
MNM1D		X	D	P	X				X	B-13
Li et al. (2008)		X	D	P	X					B-16
Liu et al. (2009)		X	P	P	X					B-19
Cullen et al. (2009)		X	D	P	X		X	X		B-21
TOUGH2		X	D	P		X	X	X	X	B-24
HYDRUS		X	D	P		X	X	X	X	B-27
Multimedia Models										
Boxall et al. (2007)		X	D	P						B-30
Blasér et al. (2008)		X	D	P	X					B-33
Mueller and Nowack (2008)		X	D	S	X					B-37
Gottschalk et al. (2009)		X	P	S	X					B-40
Alternative Approaches										
Höck et al. (2008)	X	X	D	P			X		X	B-45
Hansen et al. (2008)		X	D	P	X			X		B-49
Linkov et al. (2007)		X	D	P	X					B-52
Linkov et al. (2009)		X	P	S	X					B-55

Surface Water Models

Mackay et al. (2006)

Summary: This model provides an approach for predicting whether nanoparticle suspensions in aqueous systems will be stable – i.e., whether the particles will aggregate and settle out or remain stable in solution. The model is inherently probabilistic and results in a probability distribution for the predicted behavior. The model was developed to support the documented analysis. No other use, verification, or validation is known.

KEY REFERENCES:

Mackay, C., Johns, M., Salatas, J., Bessinger, B., Perri, M. 2006. Stochastic probability modelling to predict the environmental stability of nanoparticles in aqueous suspension. *Integrated Environmental Assessment and Management* 2(3):293-298.

CONTACT/AVAILABILITY INFORMATION:

Christopher E Mackay (mackayc@exponent.com)

Exponent, 15375 Southeast 30th Place, Suite 250, Bellevue, Washington 98007, USA

PURPOSE AND SCOPE:

What is the model purpose? This model is designed to predict whether nanoparticle suspensions will be stable in aqueous systems – i.e., whether the particles will aggregate and settle out or remain in a stable solution.

What processes are simulated? The model considers buoyancy, aggregation, settling of nanoparticles in solution.

What are the primary assumptions? Insufficient information is available to document the model assumptions.

What transport media are considered? Aqueous solutions are considered in this model.

What spatial and temporal scales does the model consider? The scales are unspecified, however it could be any scale at which a nanoparticle aqueous suspension may be present.

What are the forms of results produced? The primary model result is the probability that a nanoparticle suspension will be stable in aqueous solution.

EVALUATION:

Background and History

How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

What physical and chemical properties are considered? The model inputs include: fluid column height, nanomaterial density, aggregation rate constant, dissociation constant, number of particles, probability of aggregation per collision, particle radius, temperature, particle volume, and fluid viscosity.

What is the mathematical representation? The model evaluates the critical buoyancy properties using the Botzmann equation and potential aggregate settling using the Stokes-Einstein equation. Kinetic aggregation is treated as a chain of binary reactions characterized by an aggregation rate constant. The model implements a stochastic Monte Carlo solution and predicts a probability distribution of apparent solubilities for nanoparticle suspensions.

What are the data requirements? The model input parameters are not extensive, however many of the parameters (e.g., aggregation rate constant) are likely unavailable currently for most nanoparticle solutions, particularly in environmental conditions (e.g., non-ideal aqueous mixtures).

Consideration of Uncertainty

*How does the model account for uncertainty***?** The model is implemented within a stochastic Monte Carlo framework and thus inherently considers uncertainty. However, given that input data are unavailable for many nanomaterials and natural conditions, realistic uncertainty predictions may not be possible in most cases.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? This model was developed specifically to evaluate nanoparticle specific behavior in aqueous systems. However, the model assumes ideal conditions and input parameter knowledge that currently significantly limit its use for evaluating many environmental nanomaterial transport problems.

How does the model address input data gaps associated with many traditional models? The model accounts for key processes of nanoparticle stability and allows user-specification of associated inputs (e.g., aggregation rate constant). However, the model does not provide any guidance on parameterization for different nanomaterials. Also, it is unclear if the model can easily be updated for emerging, scientifically relevant information for nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? This model framework may be useful to incorporate into other fate and transport models in order to extend their utility to nanomaterials. For example, this modeling approach could predict the stability of nanoparticle suspensions under different environmental conditions (i.e, the effective aqueous concentration accounting for the presence of stable particles). An environmental flow model then could predict the migration of nanoparticle contaminants at the predicted effective concentration (assuming that environmental conditions do not change).

Koelmans et al. (2009)

Summary: This mass balance model was used to compare the concentrations of manufactured carbon nanoparticles (MCNPs) to naturally occurring black carbon nanoparticles (BCNPs) in aquatic sediments. The model is a relatively simple compartmental model accounting for sedimentation, burial, and degradation. The analysis concluded that MCNP concentrations in sediments are likely to be negligible relative to concentrations of BCNPs. This conclusion is possible even when considering the significant uncertainties in the estimate due to the very large magnitude difference in the estimated concentrations.

KEY REFERENCE:

Koelmans AA, Nowack B, Wiesner MR. 2009. Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments. Environ Pollut 157:1110–1116.

CONTACT/AVAILIBILITY INFORMATION:

A.A. Koelmans (bart.koelmans@wur.nl, Phone: 31 0 317 483201)

Aquatic Ecology and Water Quality Management Group. Wageningen University, PO Box 47, 6700 AA Wageningen, The Netherlands.

PURPOSE AND SCOPE:

What is the model purpose? This mass balance model is used to compare the concentrations of manufactured carbon nanoparticles (MCNPs) to naturally occurring black carbon nanoparticles (BCNPs) in aquatic sediments. This model calculates the steady state concentrations of carbon nanoparticles using the parameters of concentration in the sediment, nanoparticle sedimentation flux, sediment thickness, accumulation, and a first order removal rate of manufactured carbon nanoparticles.

What processes are simulated? This model simulates the processes of sedimentation, burial, and removal due to aggregation and degradation to calculate the concentrations of carbon nanotubes within aquatic sediments.

What are the primary assumptions? The model is characterized by three main assumptions: (1) There is a distinct, mixed biologically active layer; (2) MCNPs enter the sediment through sedimentation; (3) MCNP removal can be modeled as a first order decay process.

What transport media are considered? This model considers transport between a water column and underlying sediments.

What spatial and temporal scales does the model consider? The specific spatial and temporal scales are not specified. However, the sediment layer is assumed to be 10 cm thick.

What are the forms of results produced? The model outputs are MCNP concentrations and MCNP to BCNP weight ratios.

EVALUATION:

Background and History

How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

How many physical and chemical properties are considered? Input parameters include: sediment layer thickness, sediment accumulation rate, first-order removal rate constant, sedimentation flux of settling solids in the water column, total concentration of MCNPs in the water column, concentration of settling solids.

What is the mathematical representation? The model is a relatively simple mass balance compartmental model characterized by mass inflows and internal transformations.

What are the data requirements? To calculate the concentration of CNPs, this model requires data inputs of: (1) sediment thickness; (2) sediment accumulation rate; (3) removal rate constant; (4) sedimentation flux; (5) total CNP concentration in the water column; (6) concentration of settling solids; and (7) Conditional distribution ratio between MCNP concentration in settling particles and MCNP concentration in water. These values are presented in table 1 of the article.

Consideration of Uncertainty

How does the model account for uncertainty? The model is deterministic and does not explicitly consider uncertainty.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The model does not explicitly represent fundamental mechanisms of particulate transport (e.g., the model does not rely on DLVO theory). Rather, the model aggregates several potential mechanisms into single mass transfer and transformation rates (e.g., first order decay, settling rate). This approach allows straightforward predictions to be made. The model does not allow any theoretical estimation of behavior and instead relies completely on the reliability and accuracy of the user-specified inputs.

How does the model address input data gaps associated with many traditional models? The authors have been explicit in the basis for input parameters and have utilized several documented estimation approaches – e.g., estimates of water concentrations based on Mueller and Nowack (2008). However, the authors readily state that the results are highly uncertain due to lack of knowledge regarding nanomaterials in the environment. The model is relatively simple and should be easily updated to account for emerging, scientifically relevant information describing nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? A major conclusion of the analysis was that MCNPs are unlikely to be present in aquatic sediments at concentrations significant relative to concentrations of BCNPs.

Packman et al. (2000)

Summary: The model simulates mass exchange of colloids between a stream and a streambed. The model considers key behaviors associated with particulates, including settling and porous media filtering. The model has been applied successfully by Boncagni et al. (2009) to evaluate an experimental study of titanium dioxide nanoparticle transport.

KEY REFERENCES:

Packman, A., Brooks, N., Morgan, J. 2000. A physiochemical model for colloid exchange between a stream and a sand streambed with bed forms. *Water Resources Research*. 36: 8 2351 – 2361.

Packman, A. I., N.H. Brooks, and J. J. Morgan, Kaolinite exchange between a stream and s treambed: Laboratory experiments and validation of a colloid transport model, Water Resources Research 36: 8.

CONTACT/AVAILABILITY INFORMATION:

Aaron I. Packman (a-packman@northwestern.edu, Phone: 847-491-9902)

Department of Civil and Environmental Engineering, Northwestern University, Evanston, IL.

PURPOSE AND SCOPE:

What is the model purpose? The model simulates the mass exchange of colloids between a stream and a streambed.

What processes are simulated? The model considers bed form driven advective pore water flow driven by stream flow over the bed forms. The advective pore water flow along with sedimentation and filtering in the porous medium resulted in pumping exchange of suspended sediment between the water column and the sediments.

What are the primary assumptions? Assumptions of the model documented in the reference included: the only effect of the bedform on the flow field in the bed is to produce a sinusoidal pressure distribution at the bed surface (no erosion or resuspension of particulates); homogeneous porous medium; suspension and bedform properties do not change with time;

What transport media are considered? The model simulates mass exchange between a stream water column and underlying sediments.

What spatial and temporal scales does the model consider? The model formulation is in terms of dimensionless parameters, which theoretically should allow the approach to be used at a wide range of spatial scales.

What are the forms of results produced? The primary results of the model are predicted concentrations in the water column and in the bed sediments as well as associated mass fluxes.

EVALUATION:
Background and History
How extensively has the model been used and applied? The model used in the primary reference as well as by Boncagni et al. (2009) to evaluate the transport of titanium dioxide nanoparticles. Section 4.2.2.1 of the report describes the Boncagni (2009) modeling effort. We are not aware of uses of the model other than these two academic studies.

What verification and validation has been conducted? The initial paper documenting the model (Packman et al., 2000) was published along with a companion paper documenting a model verification effort.

Complexity

What physical and chemical properties are considered? The model input parameters include: particle diameter, particle settling velocity, dune wavelength, bedform height, filtration coefficient, porosity of bed sediment, stream width, average stream velocity, dispersion coefficient, depth of sand bed, stream depth, concentration in stream.

What is the mathematical representation? The model is developed using a series of equations characterizing advective puming theory, colloid filtration, and settling. The formulation results in an analytical expression.

What are the data requirements? There is an extensive list at the end of the document which labels all the input parameters needed for the model.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not explicitly consider uncertainty.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The model considers key behaviors of particulate transport including settling and porous media filtering. In addition, the model has been successfully applied in a study of titanium dioxide nanoparticles (Boncagni et al., 2009).

How does the model address input data gaps associated with many traditional models? The Boncagni et al. (2009) study involved calibration of the model to experimental data. The model does not provide the ability to estimate input parameters for nanomaterials without calibration. The model is also set up to be easily updated to account for emerging, scientifically relevant information regarding nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? The primary model results include predicted concentrations within surface water and underlying sediments as well as the mass flux rate between these media.

Subsurface Models

MNM1D

Summary: The model simulates one-dimensional transport of nanoparticles in porous media. The model accounts for key nanoparticle behaviors, including attachment, detachment, and blocking, as well as transient ionic strength effects. The authors have developed a unique empirical relationship for attachment, detachment, and blocking coefficients as a function of ionic strength.

KEY REFERENCES:

Tosco T., Sethi R. (2009). MNM1D: A Numerical Code for Colloid Transport in Porous Media. Implementation and Validation. *American Journal of Environmental Science* 4: 516-524.

CONTACT/AVAILABILITY INFORMATION:

Tiziana Tosco (tiziana.tosco@polito.it, Phone: +39 011-564-7670)

DITAG-Department of Land, Environment and Geotechnologies, Politecnico di Torino, C.so Duca Degli Abruzzi 24, 10129, Torino, Italy

PURPOSE AND SCOPE:

What is the model purpose? This model was developed to simulate the one-dimensional transport of nanoparticles in porous media.

What processes are simulated? The model considers potentially transient ionic strength conditions, which can impact the stability of nanoparticle suspensions. The model accounts for particle attachment and detachment using one or two linear and/or langmuirian sorption sites and first-order kinetic attachment coefficients. The model also considers potential blocking phenomena, whereby all sorption sites become occupied.

What are the primary assumptions? Information regarding model assumptions is not provided in the reference.

What transport media are considered? Transport in saturated porous media is considered for this model.

What spatial and temporal scales does the model consider? The potential spatial scale for the model is not explicitly provided, however the example problems used for verification involve small scale problems (0.1 m, similar to a laboratory column) over relatively short time periods (minutes).

What are the forms of results produced? The model predicts nanoparticle concentrations as a function of time and one-dimensional distance from the source.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? In this paper, the authors verified the model algorithms through comparisons with existing groundwater transport models (HYDRUS-1D and STANMOD).

Complexity
What physical and chemical properties are considered? Input parameters include: inlet colloid concentration, solid bulk density, dispersion coefficient, Darcy velocity, porosity, attachment and detachment coefficients, maximum attached particle concentration (for blocking), inlet salt concentration (for ionic strength effects).

What is the mathematical representation? The model is formulated using an advection-dispersion equation along with the relevant source/sink and transformation terms describing particulate transport processes along with the coupled transport of a conservative tracer (salt, for transient ionic strength effects). The model solution is implemented in Matlab using a finite difference solution to the partial differential equations.

What are the data requirements? The data requirements for each equation presented in the model are listed after the equations.

Consideration of Uncertainty
How does the model account for uncertainty? It does not consider uncertainty.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? This model was developed specifically for the simulation of nanparticle transport in porous media. The model does account for some of the key processes for nanomaterial behavior (attachment/detachment, blocking, and ionic strength effects).

How does the model address input data gaps associated with many traditional models? The model relies on an empirical relationship developed by the authors based on laboratory experiments and theoretical considerations, which estimates attachment, detachment, and blocking coefficients as a function of ionic strength. Also, the model is implemented in Matlab and likely can readily be updated as emerging, scientifically relevant information becomes available.

What kind of interpretations/predictions can be made from this model? Several of the input parameters are difficult and potentially impossible to predict a priori (e.g., attachment and detachment rates for multiple types of sorption sites). This limitation does not necessarily prevent the use of this model to evaluate environmental transport problems. However, it does indicate that the model must be calibrated to laboratory and/or environmental data in order to develop reasonable input parameter ranges.

Li et al. (2008)

Summary: The one-dimensional model of nanoparticle transport in porous media accounted for attachment and site blocking. The model was used to interpret experimental fullerene (c60) transport. The experimental results and the calibrated model results were utilized to develop correlations relating the maximum retention capacity to the flow velocity, nanoparticle size, and mean grain size of the porous medium. The authors also estimated collision efficiency factors based on their experimental and modeling results and compared them with theoretical predictions using DLVO theory. The fitted values were more than one order of magnitude greater than the theoretically predicted efficiency factors. The authors attribute this to surface heterogeneities and suggest that clean bed filtration theory may need to be modified (to consider surface heterogeneity) in order to accurately simulate nC60 transport in porous media.

KEY REFERENCES:

Li, Y. S., Y. G. Wang, K. D. Pennell, and L. M. Abriola. 2008. Investigation of the Transport and Deposition of Fullerene (C60) Nanoparticles in Quartz Sands under Varying Flow Conditions, *Environmental Science & Technology*, 42(19), 7174-7180.

CONTACT/AVAILABILITY INFORMATION:

Linda M. Abriola (linda.abriola@tufts.edu, Phone: 617-627-3237)

Department of Civil and Environmental Engineering, Tufts, University, 200 College Avenue, Medford, Massachusetts

PURPOSE AND SCOPE:

What is the model purpose? The model simulates the one-dimensional transport of nanoparticles in porous media, considering particle attachment and maximum retention (blocking). The model was utilized in the referenced study to interpret laboratory results from a study of nC60 transport in porous media.

What processes are simulated? The model considers particle advection, dispersion, attachment, and maximum retention (site blocking).

What are the primary assumptions? Model assumptions are not documented.

What transport media are considered? The model evaluates transport in saturated porous media.

What spatial and temporal scales does the model consider? The model has been utilized to evaluate laboratory data at a scale of approximately 16 cm (a laboratory column). The time scale was not specified.

What are the forms of results produced? The primary model predictions are concentrations as a function of space and time.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? Model results were compared successfully with results measured in laboratory experiments.

Complexity

What physical and chemical properties are considered? Input parameters include: inlet concentration, soil bulk density, porosity, dispersion coefficient, pore-water velocity, particle attachment rate, and the particle retention capacity.

What is the mathematical representation? The model partial differential equations are solved using a finite difference numerical approach.

What are the data requirements? Table 1 of the document outlines the data requirements for this model.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not explicitly consider uncertainty.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The model considers several key processes for particulates in porous media, including attachment and blocking.

How does the model address input data gaps associated with many traditional models? The experimental results and the calibrated model results were utilized to develop correlations relating the maximum retention capacity to the flow velocity, nanoparticle size, and mean grain size of the porous medium. It is unknown if the model can be easily updated to account for emerging, scientifically relevant information regarding nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? The authors estimated collision efficiency factors based on their experimental and modeling results and compared them with theoretical predictions using DLVO theory. The fitted values were more than one order of magnitude greater than the theoretically predicted efficiency factors. The authors attribute this to surface heterogeneities and suggest that clean bed filtration theory may need to be modified (to consider surface heterogeneity) in order to accurately simulate nC60 transport in porous media.

Liu et al. (2009)

Summary: The model was used to interpret experimental multiwalled carbon nanotube (MWCNT) transport data. The model simulates one-dimensional transport of MWCNTs in porous media. The model is based on colloid filtration theory (attachment) with an added site-blocking term. The model successfully reproduced the experimental results. Results showed that MWCNTs were relatively mobile under the higher flow rates evaluated in this study. Because these flow rate conditions are similar to conditions in a drinking water treatment system sand filter, the results suggest that augmented treatment technologies may be necessary to remove MWCNTs from drinking water.

KEY REFERENCES:

Liu, X. Y., D. M. O'Carroll, E. J. Petersen, Q. G. Huang, and C. L. Anderson. 2009. Mobility of Multiwalled Carbon Nanotubes in Porous Media. *Environmental Science & Technology*, 25 43(21), 8153-8158.

CONTACT/AVAILABILITY INFORMATION:

Denis M. O’Carroll (docarroll@eng.uwo.ca, Phone: 519-661-2193)

Department of Civil and Environmental Engineering, University of Western Ontario, London, ON, Canada N6A 5B9

PURPOSE AND SCOPE:

What is the model purpose? The model was used to interpret experimental multiwalled carbon nanotube (MWCNT) transport data.

What processes are simulated? The model simulates one-dimensional transport of MWCNTs in porous media. The model is based on colloid filtration theory (attachment) with an added site-blocking term.

What are the primary assumptions? A complete set of model assumptions is not provided in the reference.

What transport media are considered? Saturated porous media

What spatial and temporal scales does the model consider? The model has been used to evaluate laboratory scale column experiments.

What are the forms of results produced? The primary model results are concentrations as a function of time and space.

EVALUATION:

Background and History

How extensively has the model been used and applied? To our knowledge, the model has not been used beyond the referenced study.

What verification and validation has been conducted? The model was successfully used to simulate measured data from laboratory experiments.

Complexity

What physical and chemical properties are considered? Input parameters include: inlet concentration, soil bulk density, porosity, dispersion coefficient, pore-water velocity, particle attachment rate, and the particle retention capacity.

What is the mathematical representation? The model is based on a finite-element solution to the underlying partial differential equations.

What are the data requirements? The data requirements are the same as the physical and chemical properties used in this model.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not explicitly account for uncertainty.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The model considers several key processes for particulates in porous media, including attachment and blocking.

How does the model address input data gaps associated with many traditional models? The model was used successfully to simulate experimental data. Beyond the conditions of the experiments, however, the model does not provide an approach or recommendations for parameterization for other nanomaterials. It is unknown if the model can be easily updated to account for emerging, scientifically relevant information regarding nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? The MWCNTs were quite mobile at the relatively high flow rates associated with the study (similar conditions that exist in sand filtration drinking water treatment systems). This results suggests that traditional filtration systems that do not incorporate additional treatment steps such as coagulation may not adequately remove MWCNTs. Under natural subsurface conditions, where pore water velocities would be in the lower range of those used in this study, the MWCNTs are substantially less mobile. The MWCNTs employed here were specifically engineered to be stable in aqueous solutions.

Cullen et al. (2009)

Summary: This model of nanoparticle transport in porous media is based on colloid filtration theory and associated porous media filtration mechanisms. In addition, the model allows specification of a maximum particulate retention (blocking). The model was developed to support an academic study and has not been widely used or tested. The model was developed using the COMSOL Multiphysics modeling system. Key conclusions of the analysis included that carbon nanotubes were more mobile than fullerenes and that the particulate transport behavior was strongly dependent on collision efficiency and blocking factors.

KEY REFERENCES:

Cullen, E., O'Carroll, D., Yanful, E.K., Sleep, B., 2010. Simulation of the Subsurface Mobility of Carbon Nanoparticles at the Field Scale, *Advances in Water Resources*. 33: 361–371.

CONTACT/AVAILABILITY INFORMATION:

Denis M. O'Carroll (docarroll@eng.uwo.ca, Phone: 519-661-2193)

Department of Civil and Environmental Engineering, University of Western Ontario, London, ON, Canada N6A 5B9

PURPOSE AND SCOPE:

What is the model purpose? The model was developed to support an academic study of nano-fullerenes (nC60) and multi-walled carbon nanotubes (MWCNTs) and their transport in porous media.

What processes are simulated? The model simulated nanoparticle advection, dispersion, straining, attachment, and blocking in heterogeneous porous media. The model does not address straining due to increased particle aggregation (i.e., temporal changes in the particulate suspension).

What are the primary assumptions? Removal of the nanoparticles from the aqueous phase was assumed to adhere to colloid filtration theory and associated mechanisms (e.g., deposition, interception and sedimentation). The aquifer was assumed to be completely saturated and under steady-state flow conditions. The vertical to horizontal permeability ratio was assumed to be 0.5 to account for anisotropy. The top and bottom domain boundaries were subject to Type II (Neumann) no flow boundary conditions and the right and left side boundaries were subject to Type I (Dirichlet) constant head boundary conditions. No nanoparticle flux occurred across the top and bottom boundaries.

*What transport media are considered?*The model simulates transport in saturated porous media.

What spatial and temporal scales does the model consider? The model considered a two-dimensional domain of approximately 10 square meters and time scales of several days.

What are the forms of results produced? The primary results of the model include particulate concentrations with respect to time and space.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? The reference does not document any verification or validation analysis associated with this model. However, the model was implemented using the COMSOL multiphysics system, which has been subject to extensive verification and validation.

Complexity

What physical and chemical properties are considered? Input requirements for the model include: source concentration, hydraulic gradient, longitudinal and transverse dispersion, porosity, collision efficiency factor, collector removal efficiency, and the particle retention capacity.

What is the mathematical representation? The model is implemented within the COMSOL multiphysics system, which provides a finite element solution to the underlying partial differential equations.

What are the data requirements? Table 1 of the document outlines the input parameters needed for this model.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not consider uncertainty.

Availability and Usability

Is a user-friendly interface available? The model is implemented within the COMSOL Multiphysics system, which does provide a user interface.

Does the model rely on proprietary algorithms and/or use interfaces? Yes, COMSOL Multiphysics is apropprietary modeling system.

Is the documentation complete and transparent? Yes, the model is well documented within the provided reference, and the COMSOL Multiphysics system is well documented.

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? Yes, the model incorporates key processes associated with nanoparticle transport in porous media, including porous media filtering and blocking.

How does the model address input data gaps associated with many traditional models? The model accounts for particle transport processes and allows user specification of the associated inputs. However, no guidance is provided for estimating these inputs. It is unknown if the model can be easily updated to account for emerging, scientifically relevant information regarding nanomaterial behavior.

What kind of interpretations/predictions can be made from this model? Nanoparticle transport and maximum concentrations are very sensitive to collision efficiency factors and blocking factors. At present, accurate methods to predict these factors a priori from soil and nanoparticle characteristics have not been developed. For the conditions evaluated the carbon nanotubes are much more mobile than nC60 due to the smaller collector efficiency associated with carbon nanotubes. However, the mobility of nC60 increased significantly when a maximum retention capacity term was included in the model. Model results also demonstrate that, for the systems examined, nanoparticles were predicted to be less mobile in heterogeneous systems compared to the homogeneous systems with the same average hydraulic properties.

TOUGH2

Summary: The TOUGH2 simulators are recognized for their powerful simulation capabilities involving complex fluid flow and heat transfer in porous and fractured media. The TOUGH2 codes have been applied to problems ranging from Yucca mountain groundwater flow to multi-component environmental remediation. A module has been developed to support modeling of the transport of colloids in porous media. The model simulates the potential filtering of colloids through linear kinetic rate constants characterizing attachment and detachment.

KEY REFERENCES:

Pruess, K., C. Oldenburg and G. Moridis. TOUGH2 User's Guide, Version 2.0, Lawrence Berkeley National Laboratory Report LBNL-43134, Berkeley, CA, November 1999. (2.2 Megabytes)

Pruess, K. TOUGH2 - A General Purpose Numerical Simulator for Multiphase Fluid and Heat Flow, Lawrence Berkeley Laboratory Report LBL-29400, Lawrence Berkeley Laboratory, Berkeley, CA, May 1991.

Moridis, G. J., Y. S. Wu, and K. Pruess, EOS3nT: A TOUGH2 Module for the Simulation of Nonisothermal Fluid Flow and Solute/Colloid Transport in the Subsurface; LBNL Report No. 44260, August 1999

CONTACT/AVAILABILITY INFORMATION:

Karsten Pruess (K_Pruess@lbl.gov, Phone: 510-486-6732)

Senior Scientist, Earth Sciences Division, Lawrence Berkely National Laboratory

PURPOSE AND SCOPE:

What is the model purpose? TOUGH2 is a general-purpose numerical simulation program for multi-dimensional fluid and heat flows of multiphase, multicomponent fluid mixtures in porous and fractured media. Chief application areas are in geothermal reservoir engineering, nuclear waste isolation studies, environmental assessment and remediation, and flow and transport in variably saturated media and aquifers. Although primarily designed for geothermal reservoir studies and high-level nuclear waste isolation, TOUGH2 can be applied to a wider range of problems in heat and moisture transfer, and in the drying of porous materials. The TOUGH2 simulator was developed for problems involving strongly heat-driven flow. To describe these phenomena a multi-phase approach to fluid and heat flow is used, which fully accounts for the movement of gaseous and liquid phases, their transport of latent and sensible heat, and phase transitions between liquid and vapor. TOUGH2 takes account of fluid flow in both liquid and gaseous phases occurring under pressure, viscous, and gravity forces according to Darcy's law. Interference between the phases is represented by means of relative permeability functions. The code includes Klinkenberg effects and binary diffusion in the gas phase, and capillary and phase adsorption effects for the liquid phase. Heat transport occurs by means of conduction (with thermal conductivity dependent on water saturation), convection, and binary diffusion, which includes both sensible and latent heat.

What processes are simulated? Processes simulated include advection, diffusion, dispersion, equilibrium, kinetic, or combined sorption following linear, Langmuir, and/or Freundlich isotherms, radioactive decay including daughter products, linear chemical reactions, colloid filtration, and colloid-assisted solute transport.

What are the primary assumptions? Some of the assumptions include: water flow is isothermal; concentration are at a trace level without an effect on flow properties; the gas phase pressure does not deviate from the reference pressure of the system; there is no phase change.

What transport media are considered? Porous and fractured media

What spatial and temporal scales does the model consider? The spatial and temporal scales considered are flexible. The model can evaluate small or large-scale problems at variable time scales.

What are the forms of results produced? The primary results are predicted material flows and concentrations as well as and fluxes associated with the simulated system.

EVALUATION:

Background and History

How extensively has the model been used and applied? Since its introduction in 1991, TOUGH2 has been extensively utilized and applied in the academic, regulatory, and industry realms. The model has been utilized by approximately 300 organizations in over 30 countries.

What verification and validation has been conducted? The model has been associated with many verification and validation analyses.

Complexity

What physical and chemical properties are considered? The model requires many input parameters. The reader is referred to the user’s guide for additional information.

What is the mathematical representation? TOUGH2 uses an integral finite difference method for space discretization, and first-order fully implicit time differencing. A choice of either a sparse direct solver or a various preconditioned conjugate gradient algorithms is available for linear equation solution. Thermophysical properties of water are represented, within experimental accuracy, by steam table equations provided by the International Formulation Committee. The program provides options for specifying injection or withdrawal of heat and fluids. Double-porosity, dual-permeability, and multiple interacting continua (MINC) methods are available for modeling flow in fractured porous media

What are the data requirements? Section 5 of the Moridis (199) User Guide document outlines the input parameters needed for the model.

Consideration of Uncertainty

How does the model account for uncertainty? Although the model is deterministic and does not explicitly account for uncertainty, several studies have ealuated uncertainty using the model.

Availability and Usability

Is a user-friendly interface available? No GUI is available inthe public domain, however several utility programs supporting use of the model can be found here: http://esd.lbl.gov/TOUGH2/PROGRAMS/FREEPROGRAMS.html. In addtion, a proprietary user interface named PetraSim is available from Rockware, Inc. Golden, Colorado.

Does the model rely on proprietary algorithms and/or use interfaces? No, the model is in the public domain. However, a proprietary user interface named PetraSim isavailable.

Is the documentation complete and transparent? Yes. Also the source code for TOUGH2, written in standard FORTRAN77, is available from the Energy Science and Technology Software Center (ESTSC) of the U.S. Department of Energy. The LBNL group, headed by Karsten Pruess, serves as custodians of the code, and provides limited technical support.

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? Yes, the model includes a module (EOS9nT) that implements aspects of colloid filtration theory including attachment/detachment behavior. Although the model accounts for some critical processes for particulate transport in porous media, it cannot provide guidance for parameterizing the model for nanomaterials. Also, the model has been revised numerous times since its inception, demonstrating that enhancements can be made to account for emerging, scientifically relevant information.

What kind of interpretations/predictions can be made from this model? The primary model predictions include concentrations and flow rates over time as well as boundary fluid and contaminant mass fluxes.

HYDRUS

Summary: HYDRUS simulates the movement of water, heat, multiple solutes, and particulates in variably saturated porous media (unsaturated and saturated zones). In addition to key processes relevant to transport in porous media, the model utilizes colloid filtration theory to describe the attachment/detachment behavior of particulates in porous media systems. The model has been extensively used, verified, and peer reviewed. A graphical user interface is available. The 1D version of the model is public domain, however the 2D and 3D versions are proprietary.

KEY REFERENCES:

Šimůnek, J., Changming He, J. L. Pang, and S. A. Bradford, Colloid-facilitated transport in variably-saturated porous media: Numerical model and experimental verification, Vadose Zone Journal, 5, 1035-1047, 2006.

Šimůnek, J., and M. Th. van Genuchten, Using the Hydrus-1D and Hydrus-2D codes for estimating unsaturated soil hydraulic and solute transport parameters, in van Genuchten, M. Th., F. J. Leij, and L. Wu (eds.) Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media, University of California, Riverside, CA, 1523-1536, 1999.

CONTACT/AVAILABILITY INFORMATION:

Jirka SimunekJirka Simunek (Jiri.Simunek@ucr.edu, Phone: 951-827-7854)

Professor and Hydrologist, Department of Environmental Sciences, University of California Riverside, Riverside, CA 92521, USA

PURPOSE AND SCOPE:

What is the model purpose? HYDRUS simulates the movement of water, heat, multiple solutes, and particulates in variably saturated porous media (unsaturated and saturated zones).

What processes are simulated? HYDRUS considers advection, diffusion and dispersion, sorption, and degradation of up to 15 solutes. The model also simulates diffusive transport in the gas phase. In addition, HYDRUS can evaluate non-equilibrium mass transfer through two-region, dual porosity sorption formulation, which considers mobile and immobile regions of the pore space. Filtration theory is used to describe attachment/detachment behavior of particulates (viruses, colloids, or bacteria).

What are the primary assumptions? The technical reference and user guide do not provide a listing of assumptions.

What transport media are considered? Partially saturated and/or fully saturated porous media may be simulated.

What spatial and temporal scales does the model consider? The spatial and temporal scales that may be considered are flexible. The finite element mesh may be set up to conform to irregular boundaries that encompass very small or very large systems (e.g., a few centimeters or miles).

What are the forms of results produced? The primary model predictions include concentrations and flow rates over time as well as boundary water and contaminant mass fluxes.

EVALUATION:
Background and History
How extensively has the model been used and applied? From its introduction in the mid 1990's, HYDRUS has been used very extensively, primarily (though not exclusively in the environmental field to evaluate potential contaminant migration under various scenarios. A web page listing HYDRUS-related references includes well over 100 citations (http://www.pc-progress.com/en/Default.aspx?h3d-references).

What verification and validation has been conducted? The HYDRUS technical manual (2006) provides a series of comparisons with other models and with laboratory and field data. Several of the references on the HYDRUS website (http://www.pc-progress.com/en/Default.aspx?h3d-references) include model verification and validation analyses.

Complexity

What physical and chemical properties are considered? The model includes a relatively complex, spatially explicit representation of porous media. The model input includes a large number of potential parameters for a series of optional modules simulating a range of different processes (e.g., constructed wetlands design, root water uptake). The reader is referred to the user manual (2007) for additional information about the model input parameters.

What is the mathematical representation? The flow model is based on a finite element solution to Richard's equation for variably saturated flow. The transport model is based on a finite element solution to the advection-dispersion equation.

What are the data requirements? The model input includes a large number of potential parameters. The reader is referred to the user manual (2007) for additional information about the model input parameters.

Is the model linked with any corresponding input databases? We are not aware of explicit database linkages with HYDRUS, however we have not performed a comprehensive search of the extensive HYDRUS documentation and references. Given its extensive use, it would not be surprising if the model had been incorporated into a data-driven modeling system.

Consideration of Uncertainty

How does the model account for uncertainty? The model is deterministic and the graphical user interface does not appear to support uncertainty analysis. As with any deterministic model, HYDRUS could be implemented for a probability-based analysis using Monte Carlo techniques.

Availability and Usability

Is a user-friendly interface available? Yes, a user interface is available at the product website (http://www.pc-progress.com/).

Does the model rely on proprietary algorithms and/or use interfaces? The 1D version of the model and an associated user interface are in the public domain. The 2D and 3D versions of the model are proprietary.

Is the documentation complete and transparent? Yes. Also, the source code is available for the 1D code. The code for the 2D and 3D versions may not be available, because the model is proprietary.

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? Yes, the model relies on colloid filtration theory and accounts for processes of particulate attachment and detachment. The model does not appear to account for potential blocking or enhanced transport processes. The model also does not consider potentially changing aqueous chemical conditions (e.g., pH, ionic strength) which can have a profound impact on particulate dispersions.

How does the model address input data gaps associated with many traditional models? Although the model accounts for some critical processes for particulate transport in porous media, it cannot provide guidance for parameterizing the model for nanomaterials. Also, the model has been revised numerous times since its inception, demonstrating that enhancements can be made for emerging, scientifically relevant information.

What kind of interpretations/predictions can be made from this model? The primary model predictions include concentrations and flow rates over time as well as boundary water and contaminant mass fluxes.

Multimedia Models

Boxall et al. (2007)

Summary: This model develops a series of algorithms to calculate predicted environmental concentrations (PECs) of engineered nanoparticles in air, soil, and water that arise from the use of a single product containing nanoparticles. The algorithms combine to form equations to calculate PECs based on the concentration of nanoparticles within the product combined with hypothetical daily usage of the product. This simplistic approach is applied to a limited range of products, environmental compartments, and life cycle stages, thus limiting the information that can be used. The parameter values are also entered as point estimates, addressing uncertainty at a minimum thus requiring high confidence in the data used to populate the model.

KEY REFERENCES:

Boxall, A., Chaudhry, Q., Sinclair, C., Jones, A., Aitken, R., Jefferson, B., Watts, C. 2007. Current and Predicted Environmental Exposure to Engineered Nanoparticles. Central Science Laboratory, York.

CONTACT INFORMATION:

Alistair B A Boxall (abab500@york.ac.uk, Phone: 01904 434791)

Senior lecturer, Environment Department, University of York, Heslington, York, YO10 5DD

PURPOSE AND SCOPE:

What is the model purpose? This model is designed to calculate the PECs of engineered nanoparticles in air, soil, and water arising from a range of applications of products containing nanoparticles. In order to calculate the PECs, the authors develop a series of algorithms to determine master equations for PECs of air, water, and soil.

What processes are simulated? The modeled processes are broken down into the specific media they are simulated for. The model simulates dispersion and emissions for transport in air, dilution and application processes for water, and application processes for soil.

What are the primary assumptions? This model assumes that the system is in a steady state.

What transport media are considered? The model considers the media of air, water, sludge, and soil.

What spatial and temporal scales does the model consider? Spatial and temporal scales are neglected in this model.

What are the forms of results produced? This model produces point estimates for the PECs of nanomaterials in the specified environmental compartment as a result of a specific consumer product.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity
What physical and chemical properties are considered? There are no considerations of specific physical and chemical properties of the nanomaterials. Most parameter values considering nanomaterials are estimated, such as concentration levels within the product and application rates.

What is the mathematical representation? PECs within the air compartment are calculated by computational fluid dynamic models to capture the dispersion after emissions from personal hygiene products, skin care products, traffic, and industrial stack sources. The model also includes wind speeds and dilution factors in the calculations.

To calculate the PECs for water, the model uses dilution equations for direct application of nanoparticles to the surface water, application via runoff and spray drift, and application via the sewage system dependent upon the amount of wastewater produced per capita per day. These three equations combine to determine the PECs for surface water. The dilution factor is specific to the receiving water.

Soil PECs are calculated based on the processes for direct application (through remediation technologies, plant protection products, excretion of nanomedicines used in veterinary products, and from aerial deposition) and the application of sewage sludge. To calculate the PECs as a result of sludge application, the authors first calculate the PECs of the sewage sludge based on parameters for concentration of the nanoparticles within the product, daily usage, percent removed via sewage treatment, market penetration, and sludge production.

What are the data requirements? The data requirements for calculations of PECs are presented in the table below. Along with the data characteristic are a description of the data needed and the type of form the data is inputted as (e.g. probability distribution, point estimate, ranking, etc.). The model input parameters are not extensive, however many of the parameters such as application rates, concentrations, and removal fractions are likely unavailable for most nanoparticle containing products.

Data Characteristic	Type of Input	Description
Application rate(s)	Point estimate	This is the rate at which nanoparticles are applied to the environmental source. Application can be directly, via runoff, via spray drift, or via sludge.
Dimensions	Point estimate	Length, width, depth, and density of the environmental media.
Runoff	Point estimate	Fraction of the nanoparticle applied via runoff.
Spray drift	Point estimate	Fraction of the nanoparticle release in spray drift.
Nanoparticle concentration	Point estimate	Percentage of nanoparticle contained in the product being evaluated.
Daily usage	Point estimate	This represents the amount of nanoparticle emitted due to usage of the product per day.
Market penetration	Point estimate	The amount of the population using the product.
Removal percentage	Point estimate	Fraction of nanoparticle removed by sewage treatment
Wastewater amount	Point estimate	The amount of wastewater produced and applied to the environmental compartment of concern per capita per day
Dilution factor	Point estimate	The dilution factor in the receiving water
Sludge production	Point estimate	The amount of sludge produced and applied to the environmental compartment of concern per capita per day

Table. Data Requirements.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not allow for parameters to be inputted in distributional form, but rather as point estimates. The authors consider uncertainty by calculating PECs for the different concentrations of nanoparticles within the product generating a three-scenario analysis.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? This model was developed specifically for predicting environmental exposure of nanomaterials, however does not model the chemical and physical properties specific to the behaviors of nanomaterials.

How does the model address input data gaps associated with many traditional models? The data gaps associated with traditional models are not addressed in this model. The model does not include parameters for the chemical and physical properties pertinent to nanomaterial behavior so it cannot be updated with this emerging information.

What kind of interpretations/predictions can be made from this model? Because this model is a simplistic approach based on a limited range of products, life-cycle processes, and environmental compartments and processes, it is difficult to accurately calculate the PECs of air, soil, and water for engineered nanoparticles without sufficient data.

Blaser et al. (2008)

Summary: This multimedia model incorporates the use of the Rhine river model in estimating the predicted environmental concentrations (PECs) of nanomaterials in environmental compartments of an aquatic setting (sewage treatment plants, freshwaters, and freshwater sediments). However, the model has many limiting assumptions pertaining to emissions of nanomaterials, most likely generating underestimates of the actual concentrations in the environmental compartments.

KEY REFERENCES:

Blaser, S.A., Scheringer, M., MacLeod, M., Hungerbuhler, K., 2008. Estimation of cumulative aquatic exposure and risk due to silver: contribution of nanofunctionalized plastics and textiles. *Science of the Total Environment* 390, 396–409.

CONTACT/AVAILABILITY INFORMATION:

Martin Scheringer (scheringer@chem.ethz.ch, Phone: +41 (44) 632 30 62)

Senior Scientist, Safety and Environmental Technology Group, Institute for Chemical and Bioengineering, ETH Zürich, Wolfgang-Pauli-Str. 10, Room HCI G 127, CH-8093 Zürich, Switzerland

PURPOSE AND SCOPE:

What is the model purpose? The model is designed to ultimately characterize the risk of aquatic exposure of silver through 4 stages: (1) Conduct mass flow analysis of silver and emissions estimates; (2) Estimate the PEC of silver in a river system; (3) Estimate PNEC of silver; and (4) Quantify the risk.

The development of a 13 compartment mass-balance model is used to determine the flow of silver within a freshwater system, utilizing the Rhine river model to assess the flow within the river system. The model then aims to quantify the PECs of silver within the environmental compartments of STPs, freshwater, and freshwater sediments. Once the PECs are calculated, the model calculates risk quotients (PEC/PNEC) by developing PNEC estimates from the literature.

What processes are simulated? The model simulates mass flow of silver into the environment based on emission scenarios and mass balance models for correspond transport media. The processes include sedimentation, exchange, diffusion, water flow, burial, and bed load shift.

What are the primary assumptions? This model considers the emissions of engineered nanomaterials for nano-silver as the only source of silver into the river stream. This assumption neglects sources such as particulate emissions, production of silver-containing plastics and textiles, aerial deposition, and leachates. The model bases its assessment on estimated silver use in the year 2010.

What transport media are considered? This model considers transport media of natural freshwaters and freshwater sediments.

What spatial and temporal scales does the model consider? The spatial scale is selected to be the year of 2010 and the spatial domain is the 25 member countries of the European Union.

What are the forms of results produced? The results are in the form of PECs and ultimately risk quotients. These results are point estimates for each of the scenario (low, intermediate, and high)

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? The model compares its outputs to those of empirical data from 16 different sources relating to the environmental concentrations in STP, dry sewage sludge, river water, and river sediments. This comparison is presented in figure 5 of the article.

Complexity

What physical and chemical properties are considered? It is not clear what physical and chemical properties are considered in the model.

What is the mathematical representation? The emission of silver into the aquatic environment is determined by first calculating the amount of silver released into wastewaters from biocidal products (equation 1 in the article). The authors then use this output in equation 2 to calculate the amount of silver input into the natural water system. Values are calculated for all 3 emission scenarios.

PECs are estimated utilizing the Rhine river compartment model which includes moving water, stagnant water, and the top layer of the equatic sediment and displayed in figure 3 of the article. Permanent sediment is included in the representation, but is not modeled. This model incorporates the processes of water flow, bed load shift, sedimentation, burial, exchange, and diffusion. The parameter values

What are the data requirements? The data requirements for calculations of PECs are presented in the table below. Along with the data characteristic are descriptions of the data needed and the type of form the data is inputted as (e.g. range, point estimate, ranking, etc.). Model input parameters for the Rhine river model were more extensive, utilizing a range of values with a confidence factor.

Data Characteristic	Type of Input	Description
Silver emissions for into the environment	Point estimates	There were 17 different input parameters for silver emissions into the environment. These input parameters were characterized by the media in which silver was emitted (wastewater, STP, natural water, sewage sludge, solid waste, landfills, slag, fly ashes, and the atmosphere) as well as the form from which the silver came (biocidal products, other sources). These parameters were given 3 different values pertaining to the emission scenarios of minimum, intermediate, and maximum scenarios.
Emission scenario parameters	Point estimates	There were 14 input parameters pertaining to the emission scenarios which quantified the population, silver release rate, amount of silver, wastewater produced, and fraction removed during different stages of the silver life cycle.
Mass balance parameters	Range	There were 7 input parameters to model the mass balance model once the silver had entered the aquatic environment. These parameters included: (1) water flow velocity; (2) Concentration of suspended particulate matter (SPM); (3) Sediment density; (4) Porosity of sediment; (5) Settling velocity of SPM; (6) Resuspension rate; and (7) SPM-water partition coefficient.
Predicted No-Effect Concentrations	Point estimates	These values were taken from the literature and used to calculate the risk quotient in the environmental compartments of STP, freshwater, and freshwater sediments

Table. Data Requirements

Consideration of Uncertainty

How does the model account for uncertainty? The model accounts for uncertainty by conducting a three scenario analysis labeled minimum-, intermediate-, and maximum emission scenarios. The intermediate scenario considers the most probable assumptions, while the minimum and maximum scenarios consider the assumptions that lead to lower or elevated PECs. The model performs a first-order error propagation to assess the uncertainty in the model outputs. Confidence factors in some of the model inputs are used to address the uncertainty of model inputs such as those used in the mass balance models within the aquatic environment.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The chemical and physical properties for this model only pertain to the behavior of the nanomaterials within the aquatic system. Dispersivity properties (as suggested in section 2.2 of this report when considering nanomaterial behavior in aquatic systems) do not appear to be considered in the Rhine river model, so all relevant nanospecific properties are not considered in this model.

How does the model address input data gaps associated with many traditional models? Parameter values can be altered in the Rhine river model as information is made available. However, many of the values pertinent to nanomaterial behavior may not be included.

What kind of interpretations/predictions can be made from this model? The model is intended to calculate PECs and ultimately the risk characterization of silver within different environmental compartments (STPs, freshwater, and freshwater sediment). However, the model only considers nano-silver in biocidal products as the exclusive source of silver emission, neglecting other sources such as particulate emissions. Therefore, the PECs are most likely underestimates of the actual concentrations.

Mueller and Nowack (2008)

Summary: This model was the first attempt at simulating the flow of nanomaterials through the environment based on a life cycle assessment. Though much of the data required to model this flow is uncertain and estimated on best guesses or worst case scenarios, the model sets up a framework to calculate predicted environmental conditions (PECs) for environmental compartments such as air, soil, sewage treatment plants (STP), and surface waters. This framework can be built upon as scientifically relevant information on nanomaterials becomes available.

KEY REFERENCES:

Mueller, N. Nowack,. B.2008. Exposure Modeling of Engineered Nanoparticles in the Environment. *Environ. Sci. Technol*. 42, 4447—4453.

CONTACT/AVAILIBILITY INFORMATION:

Bernd Nowack (nowack@empa.ch, Phone: +41 71 2747 692)

Empa-Swiss Federal Laboratories for Materials Testing and Research, Technology & Society Laboratory, Environmental Risk Assessment and Management Group, Lerchenfeldstrasse 5, CH-9014 St. Gallen

PURPOSE AND SCOPE:

What is the model purpose? This model was designed to calculate the quantities of engineered nanoparticles in different compartments of the environment based on a life cycle assessment. Per this assessment, the model is set up to utilize material flow analysis based on the parameters of estimated worldwide production volume, allocation of the production of nanomaterial into product categories, particle release from products, and flow coefficients between environmental compartments. Ultimately the model is intended to calculate PECs such that risk quotients can be determined based on PNECs located in the literature.

What processes are simulated? The processes simulated are substance flows based on life cycle assessments and emissions into the environment based on production and product use.

What are the primary assumptions? The primary assumptions of the model were: (1) Primary compartments of air, soil, and water were considered to be homogeneous; (2) For simplicity the system was considered to be in a steady-state; (3) In the absence of real data, substance flow rates between environmental compartments were the same for all nanoparticles; and (4) Secondary compartments (i.e. sediments and groundwater) were not considered.

What transport media are considered? The transport media of air, soil, and water compartments are considered in this model.

What spatial and temporal scales does the model consider? The model is spatially representative of Switzerland and bases its parameters for flow coefficients on tons/year. However, the system is assumed to be in a steady state such that transfer coefficients can be used to calculate concentrations.

What are the forms of results produced? The model produces PEC for the three types of nanoparticles studied. These calculations are then compared to predicted no effect concentrations (PNEC) derived from the literature to estimate a possible risk quotient (PEC/PNEC). Typically, risk quotients are categorized by a threshold of 1.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

What physical and chemical properties are considered? The model is based on material flow analysis and used flow coefficients between environmental compartments to determine PECs within each compartment. It is not clear if physical and chemical properties are considered within these compartments.

What is the mathematical representation? The calculation of PEC for specific environmental compartments is determined by substance flow through waste incineration plants (WIPs) landfills, and/or sewage treatment plants (STPs). This produced point estimates for PECs dependent upon the input values into the system.

What are the data requirements? The data requirements for calculations of PECs are presented in the table below. Along with the data characteristic are descriptions of the data needed and the type of form the data is inputted as (e.g. range, point estimate, ranking, etc.). The model input parameters are not extensive, however many of the parameters such as application rates, concentrations, and removal fractions are likely unavailable for most nanoparticle containing products. Thus, the input requirements were based on worst-case scenarios in the absence of sufficient data.

Data Characteristic	Type of Input	Description
Worldwide production volumes	Point estimates	Production volumes were taken at a best guess based on the production volumes of 10 companies in Switzerland.
Allocation of the production volumes to product categories	Point estimates for weighting factors	Different product categories were assigned to a specific nanoparticle if present in that product category. Weight factors allocated how much of the total production volume was contained in that product category.
Particle release from products	Point estimates	Each nanospecific product category had 2 to 6 different release points during the life-cycle. A percentage of nanomaterial release was given to each of these release points. The compartment to which the nanomaterial was released was also specified.
Flow coefficients	Point estimates	Flow coefficients between different compartments in the model were quantified by tons/year.

Table. Data Requirements.

Consideration of Uncertainty

How does the model account for uncertainty? The model accounts for uncertainty by developing a realistic and high exposure scenario (RE- and HE scenario). The HE scenario relied on worst-case scenario estimations, which lead to higher concentrations in the environment. This two-scenario analysis was the extent of uncertainty analysis conducted.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? This model was developed to estimate PECs of nanomaterials with the lack of data concerning relevant chemical and physical properties specific to them.

How does the model address input data gaps associated with many traditional models? The model addresses data gaps associated with many traditional models by assigning flow coefficients between environmental compartments, rather than calculating the flow within each compartment, and modeling a flow-in, flow-out process. However, calculation of the flow coefficients may not include all the necessary parameters. The model can be updated as information regarding percentage of particle release from products is quantified, as well as more data that can increase the certainty of flow coefficients.

What kind of interpretations/predictions can be made from this model? This model is a simplified approach to quantifying PECs of nanomaterial based on a life cycle assessment. The framework seems applicable, but requires more certainty in the parameter values before this assessment can be used in traditional risk assessments.

Gottschalk et al. (2009)

Summary: This multimedia environmental model was designed to calculate the predicted environmental concentrations (PECs) to be used towards a quantitative assessment of the risks of nanomaterials in the environment. Because of the current data gaps surrounding nanomaterials, this model was developed to model basically any substance with a distinct lack of data concerning environmental fate, exposure, emission and transmission characteristics. Thus, by combining methods of sensitivity and uncertainty analysis, Monte Carlo simulation, and Markov Chain Monte Carlo modeling, the proposed model can realistically calculate PECs when facing significant data gaps.

KEY REFERENCES:

Gottschalk, F., Scholz, R.W., Nowack, B., 2009. Probablilistic material flow modeling for assessing the environmental exposure to compound: Methodology and an application to engineered nano-TiO2 particles. Environmental Modelling & Software 25 (2010) 320-332.

Gottschalk, F., Sonderer, T., Scholz, R., & Nowack, B.. 2010. Possibilities and limitations of modeling environmental exposure to engineered nanomaterials by probabilistic material flow analysis. *Environmental Toxicology and Chemistry*. 29, 5, 1036–1048.

Gottschalk, F., Sonderer, T., Scholz, R., & Nowack, B.. 2009. Modeled Environmental Concentrations of Engineered Nanomaterials (TiO_2, ZnO, Ag, CNT, Fullerenes) for Different Regions. *Environmental Science and Technology*. 43, 24, 9216–9222.

CONTACT/AVAILIBILITY INFORMATION:

Fadri Gottschalk (fadri.gottschalk@env.ethz.ch, Phone: +41 44 632 63 25)

ETH Zurich, Institute for Environmental Decisions (IED), CHN J 73.2, Universitätstrasse 22, 8092 Zürich

PURPOSE AND SCOPE:

What is the model purpose? The proposed exposure assessment develops its methods from a material flow analysis (MFA) modeling approach and is accomplished via the steps:
(1) characterize source and production volumes of material (compounds or chemicals);
(2) estimate the emissions of material to environmental compartments (air, sediment, soil, surface water, etc.); (3) specify the fate in the environment; and (4) derive distributions of predicted environmental concentrations (PECs) for the studied material.

The proposed PEC modeling approach combines sensitivity and uncertainty analysis, Monte Carlo (MC) simulation, Bayesian and Markov chain modeling, and is intended for cases characterized by a distinct lack of data concerning environmental fate, exposure, emission, and transmission characteristics. The simulated PECs for materials in the desired environmental compartments provide the basis for the quantitative exposure assessment and are derived from the results of the probabilistic material flow analysis (PMFA).

What processes are simulated? The model simulates the material flow of substance through 11 compartments consisting of life-cycle (production, manufacturing, and consumption), recycling, waste incineration plants, sewage treatment plants, untreated sewage, landfills, atmosphere, soil, sediments, groundwater, and surface water.

What are the primary assumptions? The model assumptions are presented in section 2.2 of the article title *system analysis*. The section presents the system flow chart to explain all of the inputs and outputs between each environmental compartment.

What transport media are considered? This model considers the transport media of air, surface water, subsurfaces, sewage treatment plants, and waste incineration plants.

What spatial and temporal scales does the model consider? The model considered the flow of engineered nanoparticles in Switzerland as a spatial scale.

What are the forms of results produced? The results of the model give distributions of PECs for different environmental compartments.

EVALUATION:

Background and History

How extensively has the model been used and applied? This method and approach has been utilized in several recent publications (Gottschalk et al. 2010, Gottschalk et al. 2009). The former is a recent follow-up in which the author addresses both the possibilities and limitations of using this particular method for modeling environmental fate and transport. Within this article, the author discusses the other models currently used to model PECs with regards to nanomaterials. Comparatively, the author justifies why this model is more useful than the models currently developed. As of yet, there have been no new authors that have used this model in their own nanomaterial risk assessment.

What verification and validation has been conducted? Due to the novelty of its design and limitations of other research in this area, this model cannot be verified using similar models.

Complexity

What physical and chemical properties are considered? The model is based on material flow analysis and used flow coefficients between environmental compartments to determine PECs within each compartment. It is not clear if physical and chemical properties are considered within these compartments.

What is the mathematical representation? A flow chart (Figure 1) of the mathematical methodology displays the steps necessary in deriving the most informative probability distributions of PECs for any material using the PMFA modeling framework. The remainder of this summary will discuss this process and the methods presented by Gottschalk which follow the steps: (1) develop a system model with a corresponding general system of linear equations to describe the flow model; (2) use a probabilistic Monte Carlo method to determine a probability distribution of the PECs in selected environmental compartments; (3) utilize Markov chain

Monte Carlo algorithms based on the previous findings to more accurately determine the probability distribution of the PECs; and (4) perform sensitivity on the PMFA to give the risk manager more insight on the model.

Steps 1 through 3 of the methodology conceptualization are followed to develop a system design of the desired mass balance compartment flow model which specifies the compartments/processes in which the material will flow through and the directional flows associated with them. Often, a flow chart is prepared to aid in the visual understanding of the model as well as the mathematical formulation. The compartments or processes represent the different stages of material flow and directional flows represent the transfer coefficients of material. Transfer coefficients imply the transport of material between and within the compartments.

If all transfer coefficients of the material are known (or estimated by point values), the flow of the material in the system can be determined mathematically through a stationary input-output model of a set of *n* linear equations containing *n* unknowns. Matrix algebra can be used in this case and solutions for PECs can be found deterministically by computing inverse matrices. However, if transfer coefficients are not known, a probabilistic approach must be used to capture the uncertainty of these values. Density functions that represent the uncertainty of transfer coefficient values will be used in the probabilistic methods used to determine PECs for the desired environmental compartments.

Before the probabilistic methods are employed, a system of linear equations must be defined which calculates flows to and deposition within the examined compartments of the system. This system follows the balance principle that the mass of all inputs into a process equals the mass of all outputs of the process and includes accumulation or depletion of mass within the compartment. The balance principle is used to define the transfer coefficients between each compartment. Matrix algebra, input values of transfer coefficients, and values of periodic input of material to specified compartments are then combined to define a matrix equation that can solve the steady-state of the desired system of linear equations. As mentioned, point estimates of the input parameters can be used to solve the system straightforwardly and may be done for model validation (MFA standard).

Once the system of linear equations has been determined, the study employs a probabilistic determination of the unknown output variables (storage of material within the processes) via Monte Carlo (MC) methods. The MC methods in this study follow two steps: (1) model the probability distributions of all model input parameters (transfer coefficients); and (2) a repeated computation of a proposed linear equation system to determine the output variables. The first step determines a sequence of random variables for each model input parameter following a desired probability distribution (picked to represent the probability that the input parameter falls within a particular interval). The second step solves the new system of linear equations that result from these input parameters. At the conclusion of the MC method, this algorithm has solved thousands of systems of linear equations, generating a probability distribution of the unknown output variables. This is a crucial step in the modeling procedure, because it allows the modeler to gain insight on the PECs of the studied material without a full understanding of all input parameters. By simulating this method enough (Meerschaert, 2007), we can develop a smooth probability density curve of the output variables.

To more accurately describe the probability distribution of the unknown output variables, Markov chain Monte Carlo (MCMC) methods were employed. Markov chains are discrete random processes with the Markov property (Ross, 2003). A discrete random process is defined as a system that can be in various states and changes randomly in discrete steps. The Markov property distinguishes that the probability distribution of the next step is determined only by the current state of the system, and not by the previous states of the system. The state of the system changes according to the transition probabilities of the chain. Over time, regardless of the starting state of the system, this discrete process converges to an equilibrium distribution. MCMC methods are a class of algorithms that sample from probability distributions based on constructing a Markov chain that has a desired distribution as its equilibrium distribution (stationary).

Gottschalk uses Bayesian inferences to provide posterior distributions to define what is known about unobservable model input parameters given measured or simulated data. The simulated data refers to the probability distributions of the output variables found by the MC methods above. This posterior distribution is used in the MCMC algorithms to improve upon the probability distributions of the PECs. Bayesian techniques require a proposal distribution and posterior distribution. In particular, Gottschalk utilized Metropolis algorithms (Albert, 2007) with a symmetric proposal distribution and the above posterior distribution as the stationary distribution of the Markov chain to approach the optimal input parameter values. The MCMC method is repeated until the Markov chain is considered well mixed, or close to its steady state solution.

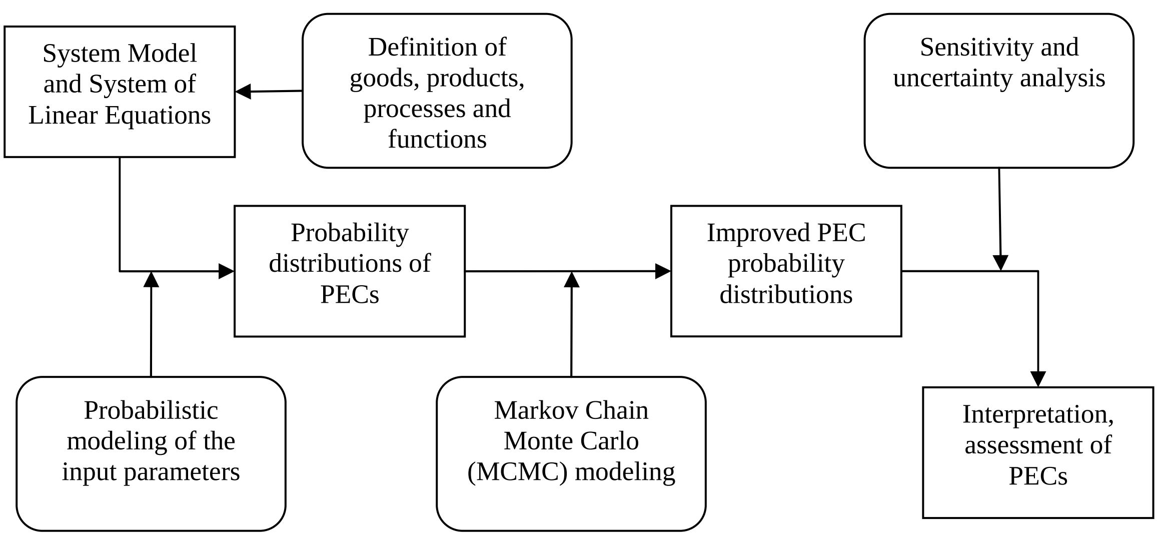

Figure 1. Basic flow chart of the PMFA methodology.

What are the data requirements? Table 3 of the Gottschalk et al. (2009) reference 30 modeling parameters needed for the model. Each parameter is inputted as a probability density function.

Is the model linked with any corresponding input databases? Currently, the model is not linked with any input databases, but potentially could be developed to utilize an input database.

Consideration of Uncertainty

How does the model account for uncertainty? A probabilistic approach is employed capture the uncertainty of transfer coefficient values. Uncertainty in the model is addressed by assigning probability density functions to determine transfer coefficient values. The (drawn) values are used in the probabilistic methods detailed above to calculate PECs for the desired environmental compartments.

Sensitivity analysis is conducted on the model to determine which input parameters have the greatest influence on output variables. This analysis allows the risk manager more information of the model at hand. Identifying the most influential parameter inputs will help the risk manager prioritize which inputs should be studied in order to reduce the uncertainty of the model and improve the overall exposure modeling process.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? This model was designed to specifically model nanomaterials. Though the model does not explicitly model the relevant physical and chemical properties needed to model nanomaterial behavior, it does employ probabilistic and Bayesain approaches to capture these behaviors.

How does the model address input data gaps associated with many traditional models? The model addresses an overall lack of data by utilizing a probabilistic and Bayesian approach to develop a probabilistic material flow analysis to quantify the output variables. The model parameters can be updated to account for relevant information regarding nanomaterial behavior, thus more accurately describing the steady state of the system.

What kind of interpretations/predictions can be made from this model? This model allows for a calculation of PECs in different environmental compartments in a steady-state system. From this assessment, risk managers would be able to calculate risk quotients of nanomaterials by obtaining predicted no effect concentrations PNECs.

Alternative Approaches

Höck et al. (2008)

Summary: The precautionary matrix serves as a guide to determine the potential health concern of nanorelavent materials in the absence of extensive data. Though this safety matrix in no way replaces the traditional risk assessment methods, it does allow a pre-characterization of potential risks and non-risk nanomaterials.

KEY REFERENCES:

Höck J., Hofmann H., Hörner K., Krug H., Lorenz C., Limbach L., Nowack B., Riediker M., Schirmer K., Som C., Stark W., Studer C., von Götz N., Wengert S., Wick P.: Guidelines on the Precautionary Matrix for Synthetic Nanomaterials. Federal Office for Public Health and Federal Office for the Environment, Berne 2008.

The PDF version of the guidelines can be downloaded from http://www.bag.admin.ch/themen/chemikalien/00228/00510/05626/index.html?lang=en.

CONTACT/AVAILABILITY INFORMATION:

Jürgen Höck (juergen.hoeck@temas.ch, Phone: +41 71 446 50 30)

Federal Office of Public Health FOPH, CH-3003 Bern

PURPOSE AND SCOPE:

What is the model purpose? The precautionary matrix is a safety matrix developed for the Swiss action plan for synthetic materials. The safety matrix is intended to estimate "nanospecific precautionary need" of synthetic nanomaterials and their applications for employees, consumers, and the environment. The model is intended to facilitate communication between all interest groups, increasing responsibility in the development of nanotechnology. However, it should be noted that the safety matrix does not substitute for an actual risk assessment. Rather than evaluating the dangers and risks associated with specific nanoparticles, this model should only be used to identify key areas for action (which may include an extensive risk assessment).

What processes are simulated? This model calculates values for nanorelevance, specific framework conditions, potential effects of the nanomaterials, and potential human and environmental exposure to nanomaterials.

What are the primary assumptions? The precautionary matrix operates under two assumptions: (1) Treat all nanomaterials as if no investigations have been carried out for specific cases to allow consistently objective evaluations; and (2) In the case of data gaps, use the worst case scenario.

What transport media are considered? The precautionary matrix does not model the transport of substance through media, rather estimates the potential risk of input into the environment.

What spatial and temporal scales does the model consider? The precautionary matrix includes the life cycle of the nanomaterial based on user inputs. The spatial and temporal scales are specific to each nanomaterial, as well as the input of the user.

What are the forms of results produced? The precautionary matrix produces a risk value based on a function of the nanorelevance, specific framework conditions, potential effect of the nanomaterial, and potential human and environmental exposure of the nanomaterial. This risk value is then classified as a low rating of need for nanospecific action or a need for nanospecific action.

EVALUATION:

Background and History

How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? This novel approach has not been verified by experimental or empirical data. Also, no other models have validated this construction.

Complexity

What physical and chemical properties are considered? The model considers redox activity, catalytic activity and stability of the nanomaterial. However, these values are quantified as low, medium or high and are not actually modeled.

What is the mathematical representation? The risk value of a given (nano)material is based on a function of the four modeled processes given above. This estimation of precautionary need is presented in section 5.2 of the guideline document where section 5.1 explains the sub-calculations needed for this overall estimation. Section 5.3 then classifies the estimation of precautionary need into two categories: (1) A score of 0-20 rates the nanospecific need for action as low; and (2) A score >20 suggests a need for nanospecific action (existing measures should be reviewed, further clarification undertaken, and measures to reduce the risk associated with manufacturing, use and disposal implemented in the interests of precaution).

What are the data requirements? The data requirements for calculations of nano-specific risk are presented in the table below. Along with the data characteristic are a description of the data needed and the type of form the data is inputted as (e.g. probability distribution, point estimate, ranking, etc.). The model input parameters are not extensive and, in the case of uncertainty, are based on a worst case scenario.

Data Characteristic	**Type of Input**	**Description**
Nanorelevance	Yes/No given values of 1 or 0	There are 5 parameters that determine the nanorelevance of a material. These parameters are based on particle and agglomerate sizes (e.g. does the material form agglomerate > 500nm?)
Specific framework characteristics	Yes/Partly/No given values of 0,3, or 5	There are 4 parameters that quantify the risk surrounding specific framework characteristics. These parameters quantify the data gaps in the current knowledge about the material (e.g. Is the origin of the starting materials known?)
Potential effect	Low/Medium/High given values of 1, 5, and 9	There are 3 parameter values for the potential effect of a material and they are based on the redox activity, catalytic activity, and the stability of the material. For the given nanomaterial a score of low(1), medium(5), or high(9) is given for each characteristic above.
Potential Human and Environmental Exposure	Various rankings; {0 or 1}, or {1, 5, or 9}	There are 9 parameter values to determine the potential human and environmental exposure and depend on: (a) the physical surroundings in production or application; (b) the contact per day; (c) potential input into the environment. An example parameter is frequency with which a consumer uses the nanomaterial product. It is given corresponding values to monthly(1), weekly(5), or daily(10).

Table. Data Requirements.

Consideration of Uncertainty

How does the model account for uncertainty? The model accounts for uncertainty addressing the data gaps in a separate variable in the overall risk calculation: specific framework conditions. If information is not known about the nanomaterial, the risk value is increased. If it is determined that the material is nanorelevant, and there is no knowledge about the material, then the mathematical representation will generate a value that is classified as a “need for nanospecific action” based solely on the specific framework conditions category.

Availability and Usability

Is a user-friendly interface available? The precautionary matrix excel form is downloadable from the website. The cells are programmed to calculate the individual category rankings as well as the overall risk value.

Is the documentation complete and transparent? Yes. Also, the embedded functions in the excel sheet are accessible such that they can be evaluated to determine if the source code is consistent with the documentation.

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The precautionary matrix considers redox activity, catalytic activity, and stability of nanomaterials. However, it does not model these properties, nor simulate transport in the environment.

How does the model address input data gaps associated with many traditional models? This model is used to quantify a precautionary need when developing nanomaterials. Thus, in the absence of extensive data, the precautionary matrix can serve as a tool to determine which nanomaterials may need precautionary action in development. The ability to store information and values in a precautionary matrix allows for an easy update of the matrix in the presence of emerging, scientifically relevant information.

What kind of interpretations/predictions can be made from this model? The precautionary matrix cannot be used to predict the risks of nanomaterials, however it can be used to evaluate whether or not more information should be gathered on a particular nanomaterial and the process in which it is used.

Hansen et al. (2008)

Summary: This adaptive framework model permits classification of products containing nanomaterials into categories of expected, possible, and no expected exposure, based on information not typically used for risk assessment but more accessible. Using (a) information from the Woodrow Wilson International Center pertaining to the location and concentration of nanoparticles within consumer products and (b) best estimates available or worst-case assumptions, the model estimates consumer exposure to selected nanomaterials. Though this model is not designed specifically for the environmental modeling of nanomaterials, a similar framework could be employed to generate preliminary estimates of environmental exposure.

KEY REFERENCES:

Hansen SF, Michelson ES, Kamper A, Borling P, Stuer Lauridsen F, Baun A (2008) Categorization framework to aid exposure assessment of nanomaterials in consumer products. Ecotoxicology 17:438–447.

CONTACT/AVAILABILITY INFORMATION:

Steffen Foss Hansen (sfha@env.dtu.dk, Phone +45 45251593)

Postdoc, Department of Environmental Engineering, Technical University of Denmark, DTU Bygningstorvet, Building 113, room 072, 2800 Kgs. Lyngby, Denmark

PURPOSE AND SCOPE:

What is the model purpose? This model proposes a framework to aid in exposure assessment of consumer products containing nanomaterials in the absence of traditional risk assessments. The model is designed to group nanomaterial-containing consumer products into three separate categories of: (1) expected to cause exposure; (2) may cause exposure; and (3) no expected exposure to the consumer. The model is also designed to categorize nanomaterial-containing products into groups pertaining to the: (a) chemical composition of the nanomaterial within the product; (b) location of the nanomaterial within the product; and (c) the type or class of nanomaterial within the product.

What processes are simulated? The only process simulated in this model is an exposure assessment which is based on default values and equations taken from the Technical Guidance Document (TGD) on risk assessment for existing substance (European Commission JRC 2003).

What are the primary assumptions? The primary assumption of this model is that exposure assessment of products based on nanotechnology must take into account the location of the nanomaterial in the product.

What transport media are considered? No transport media are considered in this model because it is designed to predict exposure from the use of consumer products.

What spatial and temporal scales does the model consider? Spatial and temporal scales are not included in this model. However, different life cycle stages of the consumer products are considered in the model to conduct exposure assessment (e.g. paint containing nanomaterials is evaluated for when it is in liquid form and in dried form).

What are the forms of results produced? This model gives results of exposure as point estimates in terms of mg kg^{-1} bw d^{-1}.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

What physical and chemical properties are considered? The only physical properties considered are concentration of the nanomaterial within the consumer product. However, the model uses the TGD on risk assessment for existing substances from the European Commission JRC (2003), so it is possible that more properties are considered.

What is the mathematical representation? The model calculates exposure assessments by estimating the quantity of active nanomaterial either: (a) on the skin per application of product (lotions); or (b) inhaled per application of the product. This value is given as a point estimate based on parameters such as chemical make-up of the nanomaterial, concentration of nanomaterial in the product, location of the nanomaterial in the product, and type of nanomaterial class. This value is then used to classify the product as: (1) expected to cause exposure; (2) may cause exposure; and (3) no expected exposure to the consumer. The authors stress that the estimated values should not be used as the basis for a risk assessment because many of the information needed for the exposure assessment is unavailable.

What are the data requirements? The data requirements for the categorization framework are presented in the table below. Along with the data characteristic are a description of the data needed and the type of form the data is inputted as (e.g. categorical, point estimate, ranking, etc.). The model input parameters are not extensive, however many of the parameters such as concentrations of active substance within the product are likely unavailable for most nanoparticle containing products so are estimated to generate different scenarios.

Data Characteristic	Type of Input	Description
Chemical identity	Categorical	The nanomaetials are classified by the chemical composition of the nanomaterial (e.g. silver, silica, etc.)
Product Categories	Categorical	The products are categorized into 8 different types: appliances, food and beverages, health and fitness, home and garden, automotive, cross-cutting, electronics and computers, and goods for children
Nanomaterial location	Categorical	The 3 categories to characterize the distribution of nanomaterials within the products are: bulk, surface, and particles.
Nanomaterial type	Categorical	The type of nanomaterials included one- or multiphase materials, patterned- or unpatterned films, and particles that are surface bound, suspended in liquids, suspended in solids, or free airborne particles.
Exposure assessment parameters	Point estimates	These values include amount of product used per application, respiratory rates, body weight, body area, and other parameters applicable to the use of the product in calculation of exposure.

Table. Data Requirements.

Consideration of Uncertainty

How does the model account for uncertainty? The main approach for uncertainty is to use worst-case assumptions or best estimates in the case of data gaps.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The model does not consider many nanomaterial properties. The only physical properties considered are the chemical composition of the actual nanomaterial and the type of nanomaterial, which is presented in the data requirements section.

How does the model address input data gaps associated with many traditional models? The model attempts to bypass traditional exposure assessment by using non-traditional parameters such as location of the nanomaterial in the product and concentration of nanomaterial within the product. However, some of this quantification was uncertain as well. The model design is intended to be updated as more information concerning nanomaterial location and nanomaterial concentration becomes available. However, this particular model is not intended for environmental exposure, so does not account for transport properties of nanomaterials.

What kind of interpretations/predictions can be made from this model? Currently, the model is intended for exposure rates to humans. However, it is feasible that the model could be modified to calculate the expected exposure to the environment based on the parameters presented above. Once the estimated levels are calculated, the results could be used with models for transport within the environment. This might require an extensive amount of data though.

Linkov et al. (2007)

Summary: The multicriteria decision analysis (MCDA) presented below develops a method in which to prioritize several nanomaterials according to specified management objectives by evaluating nanomaterials based on the criteria of potential health and ecological impacts, societal importance, and stakeholder preference. By assigning relative importance weights to the above criteria and ranking different nanomaterials according to these criteria, decision makers can determine which nanomaterials to pursue (whether in production or research) based on multiple avenues of evaluation.

KEY REFERENCES:

Linkov, I, Satterstrom, F.K., Steevens, J., Ferguson, E., Pleus, R. 2007. Multi-criteria decision analysis and environmental risk assessment for nanomaterials. Journal of Nanoparticle Research 9: 543-554.

CONTACT/AVAILABILITY INFORMATION:

Igor Linkov (Igor.Linkov@usace.army.mil, Phone: 617-225-0812)

Research Scientist, US Army Engineer Research and Development Center, Concord, MA

PURPOSE AND SCOPE:

What is the model purpose? This model illustrated an example of MCDA application to the problem of prioritizing several nanomaterials according to specified management objectives. Three hypothetical alternative nanomaterials were considered, each with different social and economic values as well as environmental properties and associated risks and benefits.

What processes are simulated? The processes simulated for this model are health and ecological effects based on public health effects, occupational exposure-related effects, and environmental effects, societal importance based on potential uses of the nanomaterials in manufacturing, potential uses in consumer products, and availability of alternatives, and stakeholder preference based on political, public, and scientific preferences.

What are the primary assumptions? The main assumptions of the model inherently deal with the associated risks of corresponding model criteria.

What transport media are considered? Transport media were not considered in this model.

What spatial and temporal scales does the model consider? The model does not incorporate spatial and temporal scales.

What are the forms of results produced? Based on their example, Nanomaterial #1 had the most benefits for industry, while Nanomaterial #2 and Nanomaterial #3 were more environmentally friendly, although the knowledge on the potential environmental risks and benefits of these materials was very uncertain. In their example, Nanomaterial #2 scored the highest and was thus the preferred alternative. Although Nanomaterial #1 might have been better economically and preferred socially, the decision process showed that Nanomaterial #2 was better overall because of its favorable environmental effects.

EVALUATION:
Background and History
How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study. However, MCDA has been used for multiple applications.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

What physical and chemical properties are considered? No properties are considered for this alternative approach; however there are 9 sub-criteria evaluated for the calculation of the overall score.

What is the mathematical representation? This model utilized the Analytic Hierarchy Process (AHP), one of the most widely used tools to help decision makers assign weights. In AHP, the category weightings were derived from a series of relative judgments in the form of a weightings ratio. The original AHP algorithms require assignments of the value on the scale from 1 to 9, while recent AHP adaptation allows incorporation of different scales including experimental and measurement values (Figueira et al., 2005). In their example, they assigned the weighting themselves.

Based on their relative weightings, AHP derived normalized weightings for the criteria. Sub-criteria and measures were compared and weighted in a pairwise manner similar to that for the main criteria. Once relative weightings were given for each of the sub-criteria, normalized weightings were calculated for use in scoring different alternatives (see breakdown in Table 2). The goal of the weighting process was to set absolute weights that reflect as closely as possible the relative ratings input by the user. In AHP procedures, weightings are calculated by finding the eigenvector corresponding to the highest eigenvalue of the weightings matrix. Other MCDA methods may use different procedures to elicit/calculate weights.

What are the data requirements? The data requirements for quantification of the above simulated processes values for the 9 sub-criteria needed to calculate the scores for each main criteria, followed by an overall risk score. The model input parameters are not extensive and require assignment from the decision maker. Input parameters were also assigned relative weighting to aid in the quantification of the main criteria.

Consideration of Uncertainty

How does the model account for uncertainty? The model does not consider uncertainty because the decision makers assigned all the weights and evaluation criteria values as point estimates.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The properties of nanomaterials were not included in the model.

How does the model address input data gaps associated with many traditional models? The data gaps posed by many traditional models were addressed by developing a ranking system for nanomaterials based on the criteria of health effects, social importance, and stakeholder preference. However, the model cannot be updated to account for emerging, scientifically relevant information unless it changes the ranking values for each nanomaterial as they pertain to health impacts, social importance, and stakeholder preference. For instance, if information suggesting that nanomaterial #1 was extremely harmful to the environment, the ranking assigned to that nanomaterial would be lowered.

What kind of interpretations/predictions can be made from this model? The model is designed to rank the different nanomaterials across all evaluation criteria. From this ranking, risk managers can make decisions on which nanomaterials to produce based on the relative health impacts, social acceptance, and stakeholder preference. The risk manager can also rerun the model with different weights to generate different scenarios, such that all angles of the development of nanotechnology can be examined.

Linkov et al. (2009)

Summary: This multicriteria decision analysis (MCDA) application addresses the problem of prioritizing several nanomaterials according to the potential risk to the environment. The MCDA attempts to incorporate several biological processes (bioaccumulation, bioavailability, toxic effects) as well as physical and chemical properties of nanomaterials (agglomeration, size, etc.) to categorize nanomaterials into groups of extreme-, high-, medium-, low-, and very low risk. By employing Monte Carlo methods, the MCDA explores all feasible values for criteria measurements and weights so that the robustness of nanomaterial categorization can be assessed.

KEY REFERENCES:

Linkov I, Steevens J, Chappell M, Tervonen T, Figuera JR, Merad M. (2009) Classifying Nanomaterial Risks Using Multi-Criteria Decision Analysis. In: Linkov I, Steevens JA (eds) Nanomaterials: risks and benefits. Springer, Dordrecht, pp 179—191.

CONTACT/AVAILABILITY INFORMATION:

Igor Linkov (Igor.Linkov@usace.army.mil, Phone: 617-225-0812)

Research Scientist, US Army Engineer Research and Development Center, Concord, MA

PURPOSE AND SCOPE:

What is the model purpose? This model is designed to guide developers in nanomaterial research and application as well as promote the safe use and handling of nanomaterials by employing the use of a MCDA support system. The model uses performance metrics that define: (a) toxicity and physico-chemical characteristics of nanomaterials; and (b) expected environmental impacts through the nanomaterial-containing product life cycle. This model was explored because traditional risk assessment models for chemical and biological materials may not be applicable to nanomaterials for some time.

This model uses a stochastic multicriteria acceptability analysis (SMAA-TRI) to explore all reasonable values for all model criteria parameters so as to group each product into specific risk categories. The SMAA-TRI was chosen because of its ability to address uncertainty by utilizing Monte Carlo simulations such that all possible parameter values and criteria weights could be assessed for the decision making tool. The goal of this MCDA was to rank the alternatives rather than select a single best alternative. In this case, the alternatives are the different nanomaterials and are ranked to prioritize the materials that need further study based on risk potentials.

What processes are simulated? The model simulates biological processes based on bioavailability potential, bioaccumulation potential, and toxic potential are given subjective probabilities based on the nanomaterial characteristics/properties.

What are the primary assumptions? The main assumptions of the model inherently deal with the associated risks of corresponding model criteria. For instance, a smaller-sized nanoparticle represents higher risk.

What transport media are considered? Actual transport is not considered in this model but bioaccumulation potential considers the accumulation of particles absorbed from all sources of soil, water, air, and food.

What spatial and temporal scales does the model consider? The model does not incorporate spatial and temporal scales.

What are the forms of results produced? The results of this MCDA group nanomaterials into a risk categorization of: extreme-, high-, medium-, low-, and very low risk. The analysis also quantifies the percentage of scenarios that a particular nanomaterial fell into the relevant risk category (figure 2 of the article).

EVALUATION:

Background and History

How extensively has the model been used and applied? To our knowledge, the model has only been used for the referenced study. However, MCDA has been used for multiple applications.

What verification and validation has been conducted? There is no known verification or validation of the model with experimental results or environmental data.

Complexity

What physical and chemical properties are considered? The model includes five properties of nanomaterials relevant to fate and transport: (1) agglomeration; (2) reactivity/charge; (3) Critical functional groups; (4) contaminant dissociation; and (5) particle size.

What is the mathematical representation? The intention of the model is to classify the alternative nanomaterials into the categories of: (1) extreme risk; (2) high risk; (3) medium risk; (4) low risk; or (5) very low risk. The results are shown in section 5 of the article.

What are the data requirements? The data requirements for the MCDA are presented in the table below. Along with the data characteristic are a description of the data needed and the type of form the data is inputted as (e.g. categorical, point estimate, ranking, etc.). The model input parameters are not extensive, however many of the parameters such as bioavailability potential are likely unavailable for most nanoparticle containing products so are estimated to generate different scenarios

Data Characteristic	Type of Input	Description
Extrinsic nanomaterial characteristics	Rates, categorizations, and estimates in distributional form.	The model includes data estimations for agglomeration rates, reactivity/charge, critical function groups, contaminant dissociation rates, and size. These values are in distributional form to capture the uncertainty surrounding the knowledge gaps concerning these characteristics
Biological processes	Subjective probabilities	Bioavailabilty potential, bioaccumulation potential, and toxicity potential are based on the nanomaterial characteristics given above.
Criteria weights	Probability distributions	The above inputs are given weights to develop multiple scenarios for a given nanomaterial. These weights are in distributional form to capture the uncertainty surrounding the importance of the above characteristics.

Table. Data Requirements.

Consideration of Uncertainty

How does the model account for uncertainty? The model accounts for uncertainty by conducting numerical simulations by comparing the effect of changing parameter values and criteria evaluations (weighting) on the modeling outcomes. Monte Carlo simulations quantify parameter imprecision by drawing parameter values from specified probability distributions. This method explores all feasible values for criteria measurements so that the robustness of nanomaterial categorization can be assessed.

Availability and Usability – *not applicable*

Application to nanomaterial behavior

Does the model consider relevant chemical and physical properties to capture nanomaterial behavior (specific to the media modeled)? The evaluation criteria are aimed to quantify the relevant chemical and physical properties relevant to environmental transport of nanomaterials. Although the transport of material is not modeled, the potential of transport is estimated based on this quantification.

How does the model address input data gaps associated with many traditional models? This model bypasses the data gaps associated with many traditional models not quantifying the actual values of necessary data. Rather, the model allows the decision maker to rank the importance of these data gaps. As emerging, scientifically relevant information becomes available, the decision maker will be able to alter the uncertainty levels of the model, as well as assign appropriate weights to the evaluation criteria. Thus, the decision makers will be able to make more accurate decisions about which nanomaterials need more research pertaining to risk assessment.

What kind of interpretations/predictions can be made from this model? This model is designed to rank the nanomaterials into different categories of potential risk. By categorizing them, risk managers can prioritize the research needs for current nanotechnology.

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