

Meditations on the Ubiquity and Mutability of Nano-Sized Materials in the Environment

Mark R. Wiesner,^{†,*,‡} Gregory V. Lowry,^{†,§} Elizabeth Casman,^{†,§} Paul M. Bertsch,^{†,⊥} Cole W. Matson,^{†,||} Richard T. Di Giulio,^{†,‡} Jie Liu,^{†,‡} and Michael F. Hochella, Jr.^{†,¶}

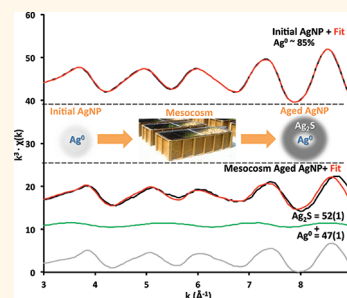
[†]Center for the Environmental Implications of NanoTechnology (CEINT), Durham, North Carolina 27708, United States, [‡]Duke University, Durham, North Carolina 27708, United States, [§]Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States, [⊥]University of Kentucky, Lexington, Kentucky 40506, United States, ^{||}Baylor University, Waco, Texas 76798, United States, and [¶]Virginia Tech, Blacksburg, Virginia 24061, United States

The doors of perception to the nanometric realm have been opened by new analytical tools that are improving our understanding of how life has evolved and how ecosystems function. Naturally occurring nanomaterials are found in a staggering range of structural and chemical variety. Because of their small size, these materials are challenging to locate, to isolate, to observe, to characterize, and/or to classify, and, just like engineered nanomaterials, their characteristics and properties can change, sometimes dramatically. The closer we look, the more it appears that particles at the nanoscale are instrumental in important geochemical and biogeochemical reactions and kinetics such as the availability of elements in the oceans,¹ the partitioning of metals in other aquatic systems,² and the bioavailability and toxicity of many elements. An examination of the potential risks to human health and the environment posed by *engineered* nanoparticles³ and the ability to construct nanophases with great precision are leading to fundamental discoveries in the ecological and life sciences.

The work by Hutchison and co-workers reported in this issue of *ACS Nano* reminds us that, in some cases, nanomaterials that are virtually identical to those we engineer can form spontaneously in nature, either from ions in solution or from larger non-nano-objects.⁴ Hutchison and co-workers describe a scenario in which metal objects that may oxidize and release class B metal cations, including silver and copper, may be subsequently photoreduced to form metallic nanoparticles. This mechanism is but one example of an untold number of nanoparticle

ABSTRACT A wide variety of nanomaterials can be found naturally occurring in the environment, although finding and characterizing these materials remains a challenge due to their size. Recent studies in the field have shown that natural nanomaterials are common in many geochemical systems. In this issue of *ACS Nano*, Hutchison and co-workers make us realize that manmade nanomaterials

can often be practically identical to those that spontaneously form in the environment. This Perspective discusses the prevalence of nanomaterials in nature, including anthropogenic and naturally occurring nanomaterials, and the dynamic behavior of these materials in the environment.



formation and growth phenomena exhibited by many of the Earth's minerals where formation conditions favor very high nucleation rates and relatively slow growth rates, resulting in many exceptionally small particles.⁵ Nanophase formation by biological processes, such as nanobiomineralization, most often involves redox reactions of aqueous species driven by bacteria and is associated with some type of cell function. Mineral weathering (breakdown under Earth surface conditions) also generates nano-sized primary or secondary phases. The observation of nanoparticle formation reported by Glover *et al.* highlights several important issues concerning nanomaterials, both naturally occurring and engineered, and the environment.

* Address correspondence to wiesner@duke.edu.

Published online November 22, 2011
10.1021/nn204118p

© 2011 American Chemical Society

The work by Hutchison and co-workers reported in this issue of *ACS Nano* reminds us that, in some cases, nanomaterials that are virtually identical to those we engineer can form spontaneously in nature.

First, the work by Glover *et al.*⁴ supports the notion that nanomaterials, defined here simply as particles that are less than 100 nm in size, are ubiquitous in the environment. Second, it underscores the dynamic nature of nanomaterial formation and transformation in the environment. The high surface-to-volume ratio of these materials makes them especially reactive in the environment, leading to a host of transformations that affect their behavior, bioavailability, and potential toxicity in the environment. In the case of engineered nanomaterials, it is the transformed material, rather than the pristine starting materials, that must be evaluated for potential impacts on the environment. Finally, this work suggests that nanophases may play a significant role in the cycling of elements in the biosphere and in biological processes. Given the extraordinary number of formation scenarios within the vast range of Earth incubators for nanomaterial generation, it is apparent that all living things, from the origin of life until today, have evolved among and always existed within and around a huge variety of nanomaterials. New tools that have been developed to observe these nanophases in the environment, cell cultures, or in organisms enable exploration of the roles of nanophase materials in

biology and the Earth's processes. Greatly simplified systems involving model engineered nanomaterials may simulate (to a degree) naturally occurring ones and inform us about naturally occurring processes, while naturally occurring processes may inform us about the potential impacts of engineered nanomaterials.

Naturally Occurring and Anthropogenic Nanomaterials Are Already Ubiquitous in the Environment.

The chemistry of the Earth is unimaginably complex: a magnificent tangled web of interdependencies of living and inanimate components that includes a vast and global array of naturally occurring nanomaterials.⁶ Naturally occurring nanomaterials are continuously forming within and distributed throughout continental soils, ground and surface waters, the oceans, and the atmosphere. We estimate that soils are the most prolific generators of Earth's nanomaterials, and that oceans provide the largest collective reservoir of these materials.⁶ Transport of soil-derived nanomaterials to the oceans occurs primarily by the world's rivers, but significant portions are also transported to the sea by glacial and aeolian (airborne) processes. By far, the largest amount of aeolian nanomaterials are lofted and transported by winds blowing over arid and semiarid lands, with a smaller contribution from agricultural lands. This far exceeds airborne nanomaterials derived from biological debris, volcanic aerosol emissions, as well as hydrous sulfate and chloride aerosol salts which condense from drying sea spray droplets. All of these aeolian nanomaterials travel the world courtesy of atmospheric circulation patterns.

The variations observed in the origin and types of naturally occurring nanoparticles is striking. For example, it has been shown that active earthquake-generating faults can produce massive quantities of nanoparticles *via* mechanical grinding.⁷ Surprisingly, this process can generate mineral nanoparticles down to 10–20 nm in size, and wide

The chemistry of the Earth is unimaginably complex: a magnificent tangled web of interdependencies of living and inanimate components that includes a vast and global array of naturally occurring nanomaterials.

swaths of these materials within highly fractured fault zones may be important in fault mechanics. Beyond Earth, spectral imagers onboard Mars Viking and Pathfinder landers as well as ground-based observations have strongly suggested the presence of nanophase ferric oxides in Martian soils and airborne dust.⁸ Finally, trace amounts of diamond nanoparticles exist within chondritic meteorites and interplanetary dust particles.⁹ These nanodiamonds average only 3 nm in diameter, with some as small as 1 nm (<150 carbon atoms). These nanodiamonds are thought to have formed either within supernovae that supplied raw materials for the formation of our solar system or perhaps directly in our sun's solar nebula and in conjunction with other star types.

Back on Earth, observations of nanoscale materials in natural waters, impacted waters (*e.g.*, mine drainage sites), and in the built environment (*e.g.*, wastewater treatment plants) are now common and include TiO₂ in mine drainage, ferrihydrite in nature and acid mine drainage sites,¹⁰ and Ag₂S in water treatment plants.¹¹ The prevalence of sources of metal nanoparticles emanating from industry, nature, or byproduct of human activity has implications for interpreting ambient concentrations, metal nanoparticle

persistence, and size distribution—important considerations in environmental risk assessment. Naturally produced nanoscale particles from sources such as forest fires, bacterial metabolism, or dissolution, as well as nanoparticles produced by precipitation in waste streams, internal combustion engines, and other “incidental” sources, must be considered alongside sources of engineered nanomaterials (ENMs). In some cases, the produced materials are virtually identical to ENMs, as in the case of fullerenes produced in engineered, natural, or incidental combustion processes. Incidental carbon nanotubes and other fullerene-related nanocrystals have been reported to originate from propane stoves, wood fires, burning tires, and other sources.^{12,13}

Nanomaterials Are Dynamic in Nature.

All nanoparticles, once released into the environment, undergo dramatic and complex transformations through interactions with various chemicals and other factors (e.g., UV light, interaction with (in)organic ligands, redox reactions, biotransformations, aggregation). Such transformations will in turn affect the nanoparticles' toxicity. A recent study demonstrated that exposure of Ag nanoparticles to sunlight induces their aggregation and greatly decreases their toxicity to a studied wetland plant, *Lolium multiflorum*.¹⁴ Similarly, exposure to sulfide at environmentally relevant concentrations affects the surface charge, aggregation state, and release of Ag ions from Ag nanoparticles.¹⁵ The oxidation of Fe(0) nanoparticles to magnetite greatly decreased their toxicity potential as determined by exposure to central nervous system glial cells and neurons.¹⁶ The adsorption of organic matter to nanoparticles, which invariably occurs in the environment, can affect their aggregation, mobility in the environment, and their toxicity potential. The organic polymeric coatings on nanoparticles may be degraded by microorganisms, resulting in aggregation and subsequent fate in the environment.¹⁷ There is also

evidence that metal atoms on nanoparticles can readily exchange with dissolved metal atoms, demonstrating the dynamic nature of the *surface* of nanoparticles. Given that a particle's surface is largely responsible for its reactivity and behavior, the dynamic, ever-changing nature of the surface cannot be overlooked.

Aggregation has been shown to affect both the dissolution rate¹⁸ and reactivity¹⁹ of nanoparticles. A direct link between structures of fullerene aggregates and the kinetics of reactive oxygen species production has been demonstrated. The underlying theory developed to predict C₆₀ and fullerol photochemistry¹⁹ is applicable to other systems in which the reactivity of nanoparticle surfaces is affected by proximity to other nanoparticles. Part of the effect of aggregation is simply to reduce mass transfer of solutes or water to particle surfaces, as has been observed in the dissolution of lead sulfide nanoparticles.²⁰ While mass transfer and shadowing effects can be expected to slow reactions on particle surfaces within an aggregate, the very proximity of reactive surfaces creates elevated *local* concentrations of reactant surfaces within aggregates relative to the bulk and determines the net reactivity when nanoparticles aggregate. The result in fullerene aggregates is an increase in triplet–triplet annihilation and triplet–ground state interactions that reduce reactivity. Changes in nanoparticle reactivity and in nanoparticle dissolution rate can be expected to alter their potential effects on organisms and persistence in the environment.

The work by Hutchison and co-workers,⁴ as well as the examples given above, highlight the importance of understanding the complex interactions between nanomaterials and the environment, including how nanomaterials could transform, what they transform into, and, perhaps most importantly, that the surfaces of the materials are ever-changing depending on the

nature of the fluid in which they are suspended. Nanomaterials must therefore be considered as highly dynamic and mutable in the environment.

Implications of Nanomaterial Transformation for Toxicity and Bioavailability.

Metals ecotoxicology research has long focused on metal speciation and equilibrium. These methods have not historically taken into account nanophase materials that can be part of the equilibrium/speciation process, even though the first reported violation of the free ion activity model for nonlipophilic metal complexes was found to be a now well-studied nanoscale Al complex, the tridecameric Al (Al₁₃) (AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺) species. This important nanocluster was initially found to be 60–100 times more toxic to plants than the “dissolved” hexaaqua Al³⁺ ion^{21,22} and later was demonstrated to be more toxic to fish, algae, and other ecoreceptors, as well. Recent evidence also suggests that plants and microorganisms may be involved in the biogenic synthesis of a wide variety of nano-sized metal, metal oxide, and metal sulfide phases.

Thus, one consequence of the formation and transformation of nanoparticles from dissolved metals is that one must account for the presence and nature of nanophases, even when nanoparticles may not be the original form of the material released. The role of nanophases in metal equilibrium processes is not currently well understood. Fundamental research is needed to adapt existing equilibrium models to account for the generation of nanomaterials from dissolved metals, the formation of nanoparticles from macroscopic objects, and to improve our understanding of how engineered nanomaterials may confound equilibrium modeling. Our models of metal toxicity are largely based on an understanding of metal speciation and equilibrium and how these factors affect bioavailability. Not accounting for the role of nanophase materials in metal

speciation and equilibrium, and thus bioavailability, could lead to an underestimation of environmental risk. Even without a unique mechanism of toxicity for nanoparticles, nanophases could contribute to greater-than-expected toxicity *via* additional routes of exposure or simply through a more efficient delivery system for toxic metal ions (e.g., a Trojan horse effect).

Fundamental research is needed to adapt existing equilibrium models to account for the generation of nanomaterials from dissolved metals, the formation of nanoparticles from macroscopic objects, and to improve our understanding of how engineered nanomaterials may confound equilibrium modeling.

Transformations can greatly impact the bioavailability and uptake of nanoparticles as well as the resulting metals released from them. Silver nanoparticles, as well as other particles made from class B metal ions such as Au, Cu, Pb, or Zn, will invariably sulfidize in most environments (e.g., in sediments, and even in air, silver objects are readily tarnished due to reaction with sulfide in the air). This sulfidation decreases the amount of Ag ions that are released from those materials, which in turn decreases their toxicity.²³ Recent work in the Center for Environmental Implications of Nanotechnology (CEINT) has

demonstrated that Ag nanoparticles indeed sulfidize over an 18 month period in a simulated wetland; however, the sulfidation is incomplete, and, despite the very small amount of Ag ions released from the sulfidized particles, initially added metallic Ag nanoparticles remained bioavailable to plants and fish in the system. Silver nitrate added to a similar mesocosm resulted in the formation of Ag₂S particles, suggesting that class B soft metal ions are transformed over time in nature, likely to metal sulfide nanoparticles. While clear mechanisms of nanoparticle uptake by plants have yet to emerge, there is ample evidence demonstrating that a range of metal, metal oxide, and carbon-based manufactured nanomaterials can be taken up by certain plants and distributed in root, stem, and leaf tissues, although both the symptoms and the extent of damage tend to be nanomaterial-specific and variable between studies.

The ambiguous distinction between engineered, natural, and incidental nanoparticles became somewhat moot with the European Commission's recommendation in October 2011 that the term "nanomaterial" be defined as "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate, or as an agglomerate, and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm."²⁴ There is an inherent recognition in this definition that all sources of nanomaterials are important in evaluating the possible impact of nanoscale materials on human health and the environment; however, perhaps the greatest benefit to studying these materials will be in their ability to inform us about the manner in which nano-sized materials have been a part of our environment from the beginning. The study of engineered nanomaterials informs us about and facilitates our study of naturally occurring processes that reciprocally provide us clues

regarding the potential toxicity, environmental impact, and risk associated with human activities that result in the production of nanoparticles. Recognition of the dynamic nature of nanoparticles in the environment adds another dimension to an already broad definition of nanomaterials, that of mutability and transformation.

REFERENCES AND NOTES

1. Turekian, K. K. Fate of Metals in Oceans. *Geochim. Cosmochim. Acta* **1977**, *41*, 1139–1144.
2. Ditoro, D. M.; Mahony, J. D.; Kirchgraber, P. R.; Obyrne, A. L.; Pasquale, L. R.; Piccirilli, D. C. Effects of Nonreversibility, Particle Concentration, and Ionic Strength on Heavy-Metal Sorption. *Environ. Sci. Technol.* **1986**, *20*, 55–61.
3. Wiesner, M. R.; Lowry, G. V.; Jones, K. L.; Hochella, M. F. J.; Di Giulio, R. T.; Casman, E.; Bernhardt, E. S. Decreasing Uncertainties in Assessing Environmental Exposure, Risk, and Ecological Implications of Nanomaterials. *Environ. Sci. Technol.* **2009**, *43*, 6458–6462.
4. Glover, R. D.; Miller, J. M.; Hutchison, J. E. Generation of Metal Nanoparticles from Silver and Copper Objects: Nanoparticle Dynamics on Surfaces and Potential Sources of Nanoparticles in the Environment. *ACS Nano* **2011**, *10*, 1021/nn2031319.
5. Hochella, M. F. J.; Lower, S. K.; Maurice, P. A.; Penn, R. L.; Sahai, N.; Sparks, D. L.; Twining, B. S. Nanominerals, Mineral Nanoparticles, and Earth Systems. *Science* **2008**, *319*, 1631–1635.
6. Hochella, M. F. J.; Aruguete, D.; Kim, B.; Madden, A. S., Naturally Occurring Inorganic Nanoparticles: General Assessment and a Global Budget for One of Earth's Last Unexplored Geochemical Components. In *Nature's Nanostructures*; Barnard, A. S., Guo, H., Eds.; Pan Stanford Publishing: Singapore, 2011; pp 1–41.
7. Dor, O.; Yehuda, B.-Z.; Rockwell, T. K.; Brune, J. Pulverized Rocks in the Mojave Section of the San Andreas Fault Zone. *Earth Planet. Sci. Lett.* **2006**, *245*, 642–654.
8. Morris, R. V.; Golden, D. C.; Bell, J. F.; Shaffer, T. D.; Scheinost, A. C.; Hinman, N. W.; Furniss, G.; Mertzman, S. A.; Bishop, J. L.; Ming, D. W.; Allen, C. C.; Britt, D. T. Mineralogy, Composition, and Alteration of Mars Pathfinder Rocks and Soils: Evidence from Multispectral, Elemental, and Magnetic Data on Terrestrial Analogue, SNC Meteorite, and Pathfinder Samples. *J. Geophys. Res., [Planets]* **2000**, *105*, 1757–1817.
9. Dai, Z. R.; Bradley, J. P.; Joswiak, D. J.; Brownlee, D. E.; M., H. H. G.; Genge, M. J. Possible *In Situ* Formation of

- Meteoritic Nanodiamonds in the Earth Solar System. *Nature* **2002**, *418*, 157–159.
10. Hochella, M. F. J.; Kasama, T.; Putnis, A.; Putnis, C.; Moore, J. N. Environmentally Important, Poorly Crystalline Fe/Mn Hydrous Oxides: Ferrihydrite and a Vernadite-Like Mineral from a Massive Acid Mine Drainage System. *Am. Mineral.* **2005**, *90*, 718–724.
 11. Kim, B.; Park, C.-S.; Murayama, M.; Hochella, M. F., Jr. Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products. *Environ. Sci. Technol.* **2010**, *44*, 7509–7514.
 12. Bang, J. J.; Guerrero, P. A.; Lopez, D. A.; Murr, L. E.; Esquivel, E. V. Carbon Nanotubes and Other Fullerene Nanocrystals in Domestic Propane and Natural Gas Combustion Streams. *J. Nanosci. Nanotechnol.* **2004**, *4*, 716–718.
 13. Murr, L. E.; Bang, J. J.; Esquivel, E. V.; Guerrero, P. A.; Lopez, D. A. Carbon Nanotubes, Nanocrystal Forms, and Complex Nanoparticle Aggregates in Common Fuel–Gas Combustion Sources and the Ambient Air. *J. Nano. Res.* **2004**, *6*, 241–251.
 14. Cheng, Y. W.; Yin, L. Y.; Lin, S. H.; Wiesner, M.; Bernhardt, E.; Liu, J. Toxicity Reduction of Polymer-Stabilized Silver Nanoparticles by Sunlight. *J. Phys. Chem. C* **2011**, *115*, 4425–4432.
 15. Levard, C.; Reinsch, B. C.; Michel, F. M.; Oumahi, C.; Lowry, G. V.; Brown, G. E. Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution: Impact on Dissolution Rate. *Environ. Sci. Technol.* **2011**, *45*, 5260–5266.
 16. Phenrat, T.; Long, T. C.; Lowry, G. V.; Veronesi, B. Partial Oxidation (“Aging”) and Surface Modification Decrease the Toxicity of Nanosized Zerovalent Iron. *Environ. Sci. Technol.* **2009**, *43*, 195–200.
 17. Kirschling, T. L.; Golas, P. L.; Unrine, J. M.; Matyjaszewski, K.; Gregory, K. B.; Lowry, G. V.; Tilton, R. D. Microbial Bioavailability of Covalently Bound Polymer Coatings on Model Engineered Nanomaterials. *Environ. Sci. Technol.* **2011**, *45*, 5253–5259.
 18. Elzey, S.; Grassian, V. H. Agglomeration, Isolation and Dissolution of Commercially Manufactured Silver Nanoparticles in Aqueous Environments. *J. Nanopart. Res.* **2010**, *12*, 1945–1958.
 19. Hotze, E. M.; Bottero, J. Y.; Wiesner, M. R. Theoretical Framework for Nanoparticle Reactivity as a Function of Aggregation State. *Langmuir* **2010**, *26*, 11170–11175.
 20. Liu, J.; Aruguete, D.; Jinschek, J. R.; Rimstidt, J. R.; M.F. Hochella, J. Insights into Mineral Dissolution Rates as a Function of Grain Size, Shape, and Aggregation State. *Geochim. Cosmochim. Acta* **2008**, *72*, 5984–5996.
 21. Parker, D. R.; Kinraide, T. B.; Zelazny, L. W. On the Phytotoxicity of Polynuclear Hydroxy–Aluminum Complexes. *Soil Sci. Soc. Am. J.* **1989**, *53*, 789–796.
 22. Shann, J. R.; Bertsch, P. M. Differential Cultivar Response to Polynuclear Hydroxo–Aluminum Complexes. *Soil Sci. Soc. Am. J.* **1993**, *57*, 116–120.
 23. Choi, O.; Cleuenger, T. E.; Deng, B. L.; Surampalli, R. Y.; Ross, L.; Hu, Z. Q. Role of Sulfide and Ligand Strength in Controlling Nanosilver Toxicity. *Water Res.* **2009**, *43*, 1879–1886.
 24. Draft recommendation of the European Commission, Brussels, 2011.