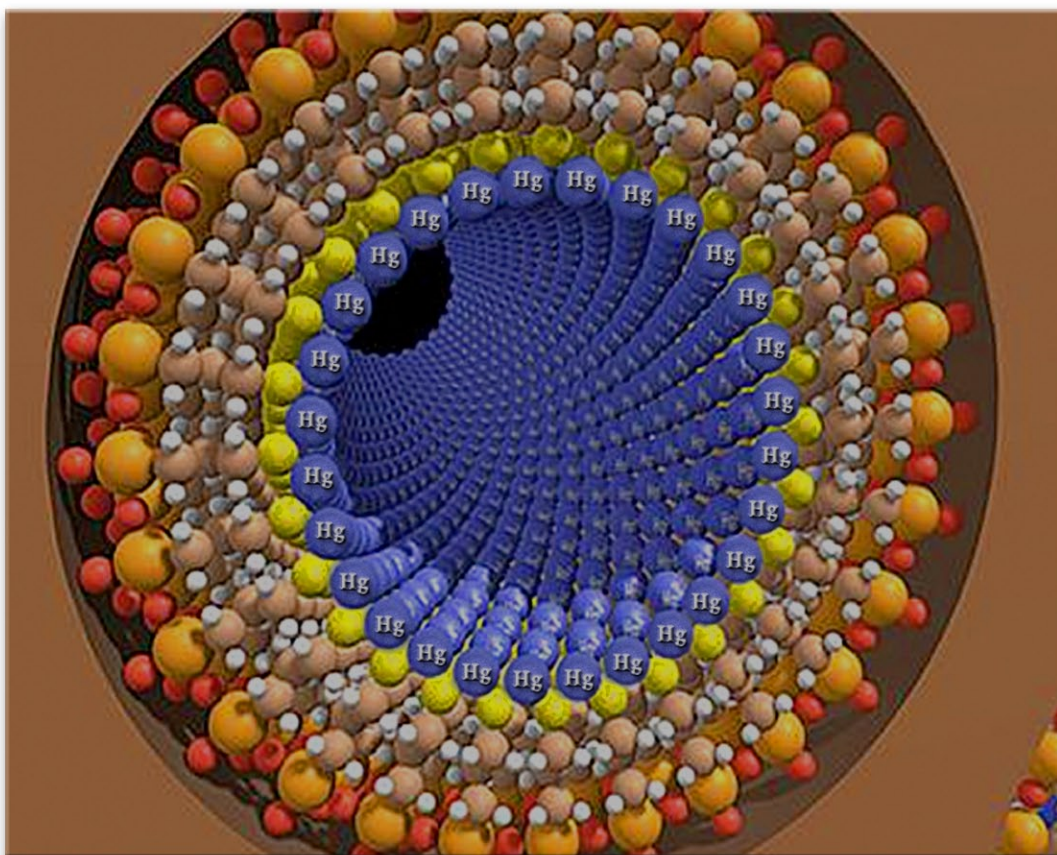


# Proceedings of the Nanotechnology Site Remediation Workshop



September 6 - 7, 2006



# **Proceedings of the Nanotechnology for Site Remediation Workshop**

**September 6-7, 2006  
United States Environmental Protection Agency, Region 5  
Chicago, Illinois**

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The artist rendition of the molecular structure of Mercury-bound SAMMS on the cover was used with the permission of Dr. Shas Mattigod, PNL.

## List of Acronyms Used

ARAR	applicable or relevant and appropriate requirement
BNP	bimetallic nanoscale particle
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
DCA	dichloroethane
DCE	dichloroethene
Dept.	department
DfE	design for environment
DNAPL	dense non-aqueous phase liquid
DOE	Department of Energy
DOD	Department of Defense
EH&S	environmental health and safety
EPA	United States Environmental Protection Agency
EZVI	emulsified zerovalent iron
FET	field effect transistor
GAC	granular activated carbon
LCA	life cycle assessment
MCL	maximum contaminant level
MFA	materials/substance flow analysis
MRNIP	modified reactive nanoscale iron particle
MWNT	multi-wall nanotube
NAES	Naval Air Engineering Station
NAPL	non-aqueous phase liquid
NAS	Naval Air Station
NCER	National Center for Environmental Research
nZVI	nanoscale zerovalent iron
ORD	Office of Research and Development
OSP	Office of Science Policy
OSRTI	Office of Superfund Remediation and Technology Innovation
OSWER	Office of Solid Waste and Emergency Response
P2	pollution prevention
PAH	polycyclic aromatic hydrocarbon
PCE	perchloroethene
ppb	parts per billion
ppm	parts per million
PRB	permeable reactive barrier
psi	pounds per square inch
R5	Region 5
RCRA	Resource Conservation and Recovery Act
RNA	ribonucleic acid
RNIP	reactive nanoscale iron particle
RPM	remedial project manager
SAMMS	self-assembled monolayers on mesoporous silica
SETAC	Society of Environmental Toxicology and Chemistry
SFD	Superfund Division

SVOC	semi-volatile organic compound
SWNT	single wall nanotube
TCA	trichloroethane
TCE	trichloroethene
TIFSD	Technology Innovation and Field Services Division
Univ.	university
VC	vinyl chloride
VOC	volatile organic compound
ZVI	zerovalent iron

## **PREFACE**

During October 2004, the United States Environmental Protection Agency (EPA) held a successful 2-day national Superfund nanotechnology site remediation conference, with assistance from partner federal agency cosponsors. This initial conference was held in Washington, DC. The conference had plenary and breakout sessions where experts in nanotechnology site remediation partook in platform presentations and panel discussions.

The 2004 conference was followed in 2006 with a 2-day national site remediation workshop, jointly sponsored by the EPA Region 5 (R5) and the EPA Office of Research and Development (ORD). This workshop is the subject of these Proceedings and targeted Superfund remedial project managers (RPMs) at the R5 offices in Chicago, Illinois. The workshop was attended by close to 100 participants. During the first day, the workshop focused on nanomaterials applications to remediate hazardous waste sites, whereas during the second day, the focus was on environmental implications of nanomaterials.

# Table of Contents

## SEPTEMBER 6, 2006

<b>Welcome to the Workshop.....</b>	<b>1</b>
Charles Maurice - <i>EPA ORD-OSP/R5-SFD</i>	
Warren Layne - <i>EPA R5-SFD</i>	
Rick Karl - <i>EPA R5-SFD</i>	
<b>Introduction to Nanotechnology for Site Remediation.....</b>	<b>1</b>
Wei-Xian Zhang – <i>Dept. of Civil &amp; Environmental Engineering, Lehigh Univ.</i>	
<b>Worldwide Nanotechnology Status.....</b>	<b>2</b>
Barbara Karn - <i>EPA ORD-NCER</i>	
<b>Cases of Nanotechnology Use at Superfund Sites.....</b>	<b>4</b>
Martha Otto - <i>EPA OSWER-OSRTI</i>	
Mary Logan - <i>EPA R5-SFD</i>	
<b>Panel Session 1: Zerovalent Iron Nanoparticles.....</b>	<b>9</b>
Wei-Xian Zhang – <i>Dept. of Civil &amp; Environmental Engineering, Lehigh Univ.</i>	
Paul Tratnyek – <i>Dept. of Environmental &amp; Biomolecular Systems, Oregon Graduate Institute of Science &amp; Technology</i>	
Krishna Reddy – <i>Dept. of Civil &amp; Materials Engineering, Univ. of Illinois at Chicago</i>	
<b>Panel Session 2: Various Nanoparticles.....</b>	<b>12</b>
Erica Forzani – <i>Dept. of Electrical Engineering &amp; Center for Solid State Electronics Research, Arizona State Univ.</i>	
Shas Mattigod – <i>DOE Pacific Northwest National Laboratory, Applied Geology &amp; Geochemistry</i>	

## SEPTEMBER 7, 2006

<b>Nanotechnology Life-Cycle Analysis.....</b>	<b>14</b>
Barbara Karn - <i>EPA ORD-NCER</i>	
<b>Risk Assessment of Nanotechnology.....</b>	<b>16</b>
Aatish Salvi - <i>Vice President, Nanobusiness Alliance</i>	
<b>Panel Session 3: Nanotechnology Risks.....</b>	<b>18</b>
Greg Lowry – <i>Dept. of Civil &amp; Environmental Engineering, Carnegie Mellon Univ.</i>	
Shane Journey – <i>Univ. of Saskatchewan</i>	
Joyce Tsuji - <i>Exponent, Health &amp; Science Practice</i>	
Fionna Mowat - <i>Exponent, Health &amp; Science Practice</i>	



**Panel Session 4: Human Health Impacts.....22**

Yvan Wenger - *School of Public Health, Univ. of Michigan*

Olivier Jolliet - *Dept. of Environmental Health Sciences, Univ. of Michigan*

Martin Philbert - *School of Public Health, Univ. of Michigan*

**ATTACHMENT 1: Workshop Agenda**

**ATTACHMENT 2: Speaker Biographies**

**ATTACHMENT 3: Participant List**



**SEPTEMBER 6, 2006**

## **Welcome to the Workshop**

Workshop co-chairs, Drs. Charles Maurice (EPA ORD-OSP/R5-SFD) and Warren Layne (EPA R5-SFD), welcomed the participants to Chicago and to the Nanotechnology for Site Remediation Workshop. Dr. Maurice explained that the two major goals of the workshop were to (1) identify how nanotechnology can be used at Superfund and Resource Conservation and Recovery Act (RCRA) hazardous waste sites; and (2) explore potential environmental implications associated with the use of nanotechnology. Dr. Maurice also reviewed the packet materials given to each participant and outlined the agenda for the day, which included both platform presentations and panel sessions.

Mr. Rick Karl (Director, EPA R5-SFD) explained that Region 5 is the first region to host a nanotechnology environmental site remediation and risk workshop. EPA is always looking at innovative applications of new technologies to allow the development of more efficient site remediation. Applications arising from the use of nanotechnological methods and materials may provide this increased efficiency in site remediation. Mr. Karl explained that Nanotechnology involves the use of materials with at least one dimension being 1-100 nm. Because of their unique physical and chemical properties, these substances are being used in hundreds of different products already available to the public, including ski equipment, stain repellants, medicines, and cosmetics. With this new technology, however, comes the possibility of potential risks to human health and the environment, topics to be discussed on day 2 of the workshop. Mr. Karl closed by stating the EPA is interested in pilot projects as well as working with academia through the support of research grants to delve deeper into the development, understanding, and use of nanotechnology to solve environmental problems.

Dr. Maurice introduced the day's first speaker, Dr. Wei-Xian Zhang.

## **Introduction to Nanotechnology for Site Remediation**

### ***Nanotechnology for Dummies***

**Wei-Xian Zhang, Dept. of Civil & Environmental Engineering, Lehigh Univ.**

This introductory presentation began with a nanotechnology overview. The properties of nanoparticles, nanomaterials, and their structures were presented. Nanoresearch and nanotechnology are conducted at the atomic, molecular, and macromolecular levels. A nanoparticle is defined by ASTM as an object with at least one dimension in the 1-100 nanometer (nm) range. Nanotechnology is the creation and use of structures, devices, and systems that have novel properties because of their small size and very large surface area. These unique properties have a great potential to enable scientists to control and manipulate matter and energy on the atomic scale.

Nanomaterials may be classified according to the type of materials of which they are composed (i.e., metal, ceramic, glass, crystals, macromolecules, biostructures), properties (e.g.: conductivity (electrical, thermal, optical), magnetic, optical, or chemical reactivity), or applications (e.g.: electronic, chemical sensing, medical, and environmental).

The two aspects of nanotechnology of interest to the EPA are applications and implications. Applications are responsive to existing problems or proactive in preventing future problems. Applications include chemical sensing, treatment, remediation, green manufacturing, and the production of green energy. Implications are the potential consequences of interactions of nanomaterials with the environment and possible ecological and human exposure risks that may be posed by the use of nanotechnology. Expected environmental interactions of chemically synthesized nanomaterials include fate/transport/transformation, lifecycle aspects, toxicity, and exposure/bioavailability/bioaccumulation.

Some new areas of investigation in nanotechnology are: surface effects of nanomaterials, synthesis and properties of nanotubes, nanoreactors, catalytic effects, photochemical transformations, nanosensors, quantum size effects, atomic-scale gaps, and the use of electrical birefringence (EB) biopolymers and deoxyribonucleic acid (DNA) to assemble and align nanostructures (self-assembly).

Some types of nanoparticles may have a potential for harm to human health and the environment. Nanotechnology may create waste with new disposal and recycling issues, release hazardous materials into the environment, lead to biological harm by possibly penetrating and accumulating in cellular material, or facilitate transport of toxic materials in the environment. Risk identification, forecasting, communication, and education are important. It is also necessary to understand any potential gaps: 1) in knowledge: due to the highly interdisciplinary nature of nanoscale science and engineering; 2) in tools: conventional environmental labs are not equipped for nanoscale work; and 3) in education: new courses/labs/programs are necessary to educate the next generation of nanotechnology researchers.

## **Worldwide Nanotechnology Status**

### ***National Nanotechnology: Science from the Top-Down and the Bottom-Up*** **Barbara Karn, EPA ORD-NCER**

Nanotechnology is not an entirely new technology. Scientists started looking at materials at the nanoscale level in the 1980s because microscopes were developed that were capable of viewing nanoscale particles. However, it has only been in more recent years (late 1990s) that nanotechnology really began to take off.

In the context of science, physicists deal with subatomic particles and chemists deal with atoms and molecules. Many substances fit the definition of nanomaterials, so diverse industries are involved with nanotechnology (e.g., automotive, sports materials, medical, and cosmetic). Nanotechnology is an enabling technology, not one that necessarily stands alone.

It is important to keep in mind that nanotechnology does not include just a single material or class of materials, nor does it include just a single industry or industrial sector. Rather, nanotechnology converges with other technologies such as biochemistry, information technology, and cognitive sciences. Molecular manufacturing may be the ultimate nanotechnology, and has the potential to revolutionize our industries. There are, however, many fundamental issues and questions to consider and resolve. For instance, which chemicals and material forms (i.e., homogeneous, heterogeneous, crystals, agglomerates, aggregates) are the best to use for a specific application; what are the levels of risks versus benefits; what should be used as standards and how should they be made; and how should nanomaterials be measured?

Under the context of industry, it is all about nanoparticle/nanomaterial properties (e.g., size, thermal, electronic, optical, magnetic, biological, wetting, mechanical) and how they can be applied (e.g., wear protection of machinery, antifouling, corrosion protection, fabrication of biocompatible implants, ultra-thin dielectrics, photo- and electro-chromic windows). The long-term view for the national nanotechnology initiative is certainly progressive. The National Science Foundation (NSF) estimates that by 2010 to 2015 approximately \$1.1 trillion will be spent on nanotechnology. NSF predicts the following partitioning of this \$1.1 trillion estimate to be in the following fields: 31 percent materials, 28 percent electronics, 17 percent pharmaceuticals, 9 percent chemical manufacturing, 6 percent aerospace, and 9 percent other.

The course of responsible research and development of nanotechnology will proceed in one of two ways. The first is for nanotechnology to be “*inherently continuous*”, meaning current laws, institutions, science, and regulatory systems may be adequate to address the potential impacts of nanotechnology. The second option is that nanotechnology is “*inherently disruptive*”, meaning that there are novel properties that only become evident at the nanoscale. This possibility would require new, flexible approaches to quickly respond to developments.

Nanotechnology products and applications are extremely diverse. Some among the hundreds of examples are paving, painting, contaminated site remediation, self-cleaning glass, and cosmetics. A list of consumer products can be found at <http://www.nanotechproject.org>. As of September 2005, the sector distribution of approximately 1,150 nanoproducts was: 38 percent materials, 23 percent industry, 15 percent testing and measurements, 7 percent end-user products, and 2 percent biomedical applications. The following are just a few of the major companies with nanoproducts on the market today: L’Oreal, Nikon, Sony, Miller Brewing, Intel, General Motors, Southern Clay, Levi-Strauss, Nike, Toyota, DuPont, Honeywell, Revlon, and 3M. In the electronics industry, some products involved with nanotechnology include: batteries, solar cells, data memory, lightweight polymer composites, flame retardants, filters, fuel cells, laser diodes, capacitors, optical switches, and fiber optics.

On December 3, 2003, the United States Government institutionalized nanotechnology with Senate Bill 189 (S. 189), the 21st Century Nanotechnology Research and Development Act. The National Nanotechnology Initiative (NNI) invests in fundamental research to advance both the understanding of nanoscale phenomena and the facilitation of technology transfer. The White House Office of Science and Technology Policy (OSTP) is at the top of the NNI administrative structure and leads the interagency Nanoscale Science, Engineering, and Technology (NSET) Committee. The members of the NSET Committee provide feedback to their respective

independent agencies and departments. The independent agencies include the EPA, Food and Drug Administration (FDA), Consumer Products Safety Commission (CPSC), National Aeronautics and Space Administration (NASA), National Institutes of Health (NIH), National Institute for Occupational Safety and Health (NIOSH), National Institute of Standards and Technology (NIST), National Science Foundation (NSF), Office of Management and Budget (OMB), and Patent and Trademark Office (PTO). The departments include Homeland Security (DHS), Health and Human Services (DHHS), Commerce (DOC), Defense (DOD), Energy (DOE), Justice (DOJ), State (DOS), Transportation (DOT), Treasury (DOTreas), and Agriculture (USDA).

The NNI's vision is "a future in which the ability to understand and control matter on the nanoscale leads to a revolution in technology and industry." One of the major goals of the NNI is to support responsible development of nanotechnology. This "responsible development" of nanotechnology has been divided into two categories: (1) environmental, health, and safety implications, and (2) ethical, legal, and all other societal issues. Because the NNI realized that new technology innovations can bring both benefits and risks to society, they have made research on, and deliberation of, these two areas a priority (Strategic Plan, 2004). Consequently, the EPA is acting as the conscience of the NNI to protect the environment and human health.

More information about the NNI and its Strategic Plan can be found at <http://www.nano.gov>.

## **Cases of Nanotechnology Use at Superfund Sites**

### ***Nanoscale Zerovalent Iron Field-Scale and Full-Scale Studies***

#### **Martha Otto, EPA OSWER-OSRTI-TIFSD**

Nanotechnology has potential applications for site remediation that include in-situ injection of nanoscale zerovalent iron (nZVI) particles into source areas of groundwater contamination. Research shows that nanotechnology may work for contaminants such as chlorinated hydrocarbons, metals, and pesticides. We have information on over 15 field-scale studies where nZVI was tested. Two of the EPA sites with field studies being conducted in 2006 are the Tuboscope Site in Alaska and the Nease Chemical Company Site in Ohio. There are also two field studies (i.e., NASA's Launch Complex 34 in Florida and a Parris Island site in South Carolina) where nanoscale emulsified zerovalent iron (EZVI) was tested.

At the Tuboscope Site, between 1978 and 1982, workers cleaned pipes used in oil well construction. The major contaminants at this site are trichloroethane (TCA), diesel fuel, and lead. The proposed remedy in one portion of this site is injection of nZVI. The remediation objectives and goals are two-fold; (1) reduce the mobility of lead at the site and (2) reduce the concentrations of TCA and diesel fuel contaminants. A field test was conducted in August 2006, and the first round of sampling was scheduled for September 2006.

Another field study site, NASA's Launch Complex 34 in Cape Canaveral, Florida, was used as a launch site for Saturn rockets from 1960 to 1968. Rocket engines were cleaned on the launch

pad using chlorinated volatile organic compounds (VOCs), including trichloroethene (TCE). Dense non-aqueous phase liquid (DNAPL), primarily TCE, is present in the subsurface.

An EZVI demonstration was conducted beneath the Engineering Support Building. EZVI consists of a hydrophobic oil membrane that is miscible with DNAPL surrounding a mixture of nZVI and water. Research indicates that contaminant destruction is achieved via abiotic degradation by the nZVI and through biodegradation enhanced by the vegetable oil and surfactant components. At NASA's Launch Complex 34, EZVI was injected into six injection wells located along the edge of the plot and directed inwards, as well as into two injection wells located in the center, which were fully screened. Injection occurred at two discrete depth intervals in each well. Results from the field study showed a significant reduction (57 to 100 percent) of TCE in target depths within five months, significant additional reduction of TCE in groundwater samples collected 18 months after injection, and suggested longer-term TCE reduction due to biodegradation. Subsequent fieldwork indicates that better distribution of EZVI may be achieved using pneumatic fracturing or direct push rather than a pressure pulse injection method.

A third field study site, the Naval Air Station (NAS) in Jacksonville, Florida, was contaminated by former underground storage tanks (USTs). Source area contaminants include TCE, perchloroethene (PCE), 1,1,1-TCA, and 1,2-dichloroethene (1,2-DCE). Cleanup was conducted under CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) and groundwater monitoring under RCRA (Resource Conservation and Recovery Act). At this site, 300 pounds of bimetallic nanoscale particles (BNP) (99.9 percent iron, 0.1 percent palladium and polymer support) were injected at ten injection points through gravity feed. Results from this study showed that nZVI significantly reduced dissolved TCE levels in several source zone wells. There were some increases in cis-1,2-dichloroethene (1,2-DCE) and 1,1-dichloroethane (1,1-DCA). Strong reducing conditions were not achieved so substantial abiotic degradation of TCE was not accomplished – presumably, nZVI was deactivated due to mixing with oxygenated water or an insufficient amount of iron was injected.

A fourth field study site is located at the Naval Air Engineering Station (NAES) in Lakehurst, New Jersey. A pilot-scale study was conducted in 2003 and full-scale work was conducted in 2005 and 2006. PCE, TCE, TCA, cis-DCE, and vinyl chloride (VC) were the most prevalent contaminants, of which the largest amounts were found 45-60 feet below the groundwater table. Phase I of the full-scale project began in November 2005 with the application of 2,300 pounds of NBP. Subsequently, Phase II started in January 2006 and involved 500 pounds of NBP. The injection method used was direct push wells and the remedial objective was attainment of New Jersey groundwater quality standards using a combination of nZVI and monitored natural attenuation. Both groundwater and soil were treated. Initial concentrations of chlorinated VOCs were as high as 360 parts per billion (ppb) and final concentrations are still to be determined. As monitoring continues, greatly reduced contaminant levels have been observed in some groundwater monitoring wells, even to the point of groundwater quality standards attainment.

The Navy has concluded that nZVI is a promising technology for source zone treatment. Success has been achieved when a sufficient amount of iron is injected into the contaminated site to create a strongly reducing environment. It is important that care be taken so that nZVI is not

deactivated during storage or mixing. The Navy also concluded that short-term performance monitoring can be misleading and that long-term treatment zone monitoring, lasting until oxygen-reduction potential levels have returned to pre-treatment levels, is essential.

The Technology Innovation and Field Services Division (TIFSD) within the EPA Office of Superfund Remediation and Technology Innovation (OSRTI) is collecting information on sites where nZVI has been tested. Cost and performance, media and contaminants treated, technology and corresponding vendors, and points of contact are all being included among the information being collected. TIFSD is also preparing a fact sheet on the use of nanotechnology for site remediation.

***Nease Chemical Superfund Site Nanotechnology Update***  
**Mary Logan, Superfund Project Manager, EPA R5-SFD**

The Nease Chemical Superfund Site (Nease) in Ohio encompasses approximately 44 acres. The Nease facility was a chemical manufacturing plant from 1961 to 1973. Some interim cleanup has been conducted since facility activities ceased. The primary contaminants selected for remediation at this site are mirex (in the soil) and VOCs (in the groundwater). A future remedy will address sediment and floodplain contamination.

There are five former wastewater ponds (numbered 1, 2, 3, 4, and 7) that are generally filled and vegetated. Ponds 1 and 2 cover approximately 1.5 acres and are the most contaminated, with about 50,000 cubic yards of waste/fill and underlying soil. Maximum reported contaminant concentrations in Ponds 1 and 2 are: greater than 50,000 parts per million (ppm) VOCs, approximately 11,000 ppm semi-volatile organic compounds (SVOCs), approximately 1,000 ppm pesticides. NAPL is also present in waste and till. Impacts in Ponds 3 and 4 are less significant. Mirex is the primary contaminant of concern (maximum of 2,080 ppm) in the soil.

The groundwater is in several hydrogeologic units (i.e., overburden, transition bedrock, and Middle Kittanning Sandstone bedrock), all of which are hydraulically connected. Ponds 1 and 2 are the primary source of contamination to the groundwater, where waste/fill in the ponds is generally below the water table. The primary contaminants in groundwater are chlorinated ethanes and ethenes, benzene, and chlorobenzene.

The overburden groundwater consists of glacial till – silty clay with discontinuous sand at an average thickness of 20 feet. Depth to the groundwater ranges from a few feet to approximately nine feet. Velocity ranges from one to 30 feet per year. There are both eastern and southern plume components.

The bedrock groundwater consists of Middle Kittanning Sandstone ranging in thickness from 21 to 53 feet with a velocity of 65 to 160 feet per year. The bedrock is fractured, so flow primarily occurs through bedding plane partings. The plume length is approximately 1,650 feet. DNAPL is present in the bedrock groundwater near the source area and maximum total dissolved VOC concentrations are greater than 100 ppm. Natural attenuation seems to be occurring, especially downgradient.



EPA selected a remedy for soil, source areas, and groundwater in 2005. Ponds 1 and 2 will be treated *in situ* by soil mixing/air stripping, stabilization, and solidification. The other ponds and soil will be covered/capped using either an impermeable geosynthetic membrane plus soil, or only clean soil (this method will also be used on Ponds 1 and 2 after treatment). The shallow, eastern groundwater will be captured in a new collection trench, pumped above ground, and treated on site. Deep groundwater and the shallow southern area will be treated by injection of nZVI. Long-term operation, monitoring, and maintenance are needed, as well as institutional controls.

Site goals include: control of releases to groundwater via leaching from Ponds 1 and 2; runoff control; control of direct contact exposure from soil and pond waste; and reduction of groundwater contaminant concentrations to the maximum contaminant levels (MCLs).

**What nZVI is and How it Works** - nZVI preparations are 1 to 100 nanometer sized iron particles with a large surface area compared to their volume. nZVI is very reactive; contaminants are destroyed by a reaction similar to rusting and have non-toxic by-products. An iron-water slurry is injected through wells into the contaminated aquifer designed to diffuse/flow with the groundwater. Use of pressure injection and/or down gradient extraction may increase dispersion. The goal is *in situ* treatment of the contaminants.

Contaminants are rapidly destroyed by oxidation-reduction reactions. With time, iron particles partially dissolve or settle out and reactivity declines. Many changes will occur in the groundwater chemistry with nZVI treatment: oxidation-reduction potential is greatly lowered; dissolved oxygen will be eliminated; and dissolved iron will increase.

Some things to keep in mind when considering nZVI are the types of contaminants at the site and the ability of nZVI to treat the contaminants of concern, existing conditions (i.e., site hydrogeology and groundwater chemistry), source control, underground injection requirements (likely to be Applicable or Relevant and Appropriate Requirements [ARARs]), and cost. It is also necessary to estimate: (1) the number of injection wells, as the radius of influence of the treatment zone will determine spacing of the injection wells, and (2) the frequency of injections, calculated by the nZVI mass requirements.

There are several reasons nZVI was selected for the Nease facility. First, there was good baseline information regarding site hydrogeology and chemistry/geochemistry. Second, conditions were unfavorable for other remediation options due to the presence of DNAPL and fractured bedrock. Third, there were favorable geochemical conditions such as low dissolved oxygen concentrations and relatively low nitrate/nitrite and sulfate. Fourth, there is a desire to maintain/enhance site conditions that support natural attenuation; the strongly reducing conditions created by nZVI are favorable for anaerobic bacteria which will help degrade chemicals that are not treated directly. Fifth, nZVI treatment can be administered at a relatively low cost. Finally, there was agreement on pre-design needs and a cooperative technical team.

At the Nease facility, a nZVI treatability study is being conducted as part of the pre-design investigation. The nZVI study has two phases – a bench scale study and a field pilot test – the

results from which the final remedial design will be based. Site-specific objectives for the bench study (initiated in July 2006) include: assessing the effectiveness of nZVI for treatment of chlorinated VOCs; determination of the potential of nZVI to treat non-chlorinated VOCs; evaluation of by-product generation; determination of optimal formulation and dosage; evaluation of site-specific geochemical influences on treatment effectiveness; and determination of the longevity of nZVI. The bench study approach included: groundwater collection from a highly contaminated well for a baseline analysis; jar tests for rate and effectiveness of a range of nZVI concentrations/formulations (0, 0.05, 0.1, 0.5, 1, 2, 5, and 10 g/L); jar tests to assess the influence of site geology on treatment; and capacity tests to determine the effectiveness of iron to treat re-contaminated samples.

Preliminary results from the bench study show that treatment is effective for chlorinated VOCs with some formulations (e.g., iron with 1 percent palladium worked better and faster in the first two weeks and 2-5 grams per liter of iron was an effective treatment concentration). Also, no toxic chlorinated by-products were observed. Additional studies are ongoing to determine site-specific geochemical influences and longevity of nZVI.

The field pilot test was scheduled to begin in October 2006 with the objectives to verify laboratory results; evaluate treatment under field conditions (i.e., confirm in-situ treatment effectiveness, evaluate geochemical changes in the aquifer, evaluate rate of transport/dispersion of nZVI, assess size of effective treatment zone, and assess *in situ* longevity); and support the remedial design. The approach for the field pilot test includes bringing nZVI to the facility as a parent slurry, mixing the parent slurry with potable water to provide the injected slurry, and injecting the nZVI slurry into a groundwater well. Injection will occur at low pressure (approximately 30 pounds per square inch (psi)) over several days and the well will be flushed with clean water after injection. Three types of monitoring will be used for the field pilot test: installation and monitoring of three new wells, down-hole electronic data loggers, and pre- and post-injection chemical monitoring.

**Health and Safety** - Iron is abundant in nature, i.e., it makes up five percent of the Earth's crust; it is found in groundwater, soil, and surface water; and it is found with structure and size ranges similar to nZVI. The fate and transport of nZVI at the Nease facility will be limited to the plume core, as it will settle into the aquifer by sorption or agglomeration and there will be no release to surface water or surface soil. Health and safety provisions for nZVI have been included in a work plan at the site since the dust is flammable/explosive and inhalation, eye, or dermal exposures could cause adverse health effects.

**Cost** - The bench and field pilot studies are estimated to cost \$30,000 and \$100,000, respectively. Over the course of two years, the cost for the nZVI groundwater treatment component of the selected remedy is estimated to be between \$1.7 and \$2 million.

A technical memorandum for the Nease facility is to be released in 2007 and will include results of all tests, recommendations for full scale use, and lessons learned. Nanotechnology updates will be given periodically. Other information can be obtained at <http://www.epa.gov/region5/sites/index.htm#nease>.

## **Panel Session 1: Zerovalent Iron Nanoparticles**

### ***Nanoscale Iron Particles: Materials and Environmental Chemistry***

**Wei-Xian Zhang, Dept. of Civil & Environmental Engineering, Lehigh Univ.**

The concept of nZVI includes synthesis/production, characterization, geochemistry, reactivity, mobility, long-term performance, and environmental impact. nZVI is an effective reductant, widely used in permeable reactive barriers (PRBs) and is considered to be nontoxic and cheap. Synthesis is affected by stirring speed, titration rate, concentrations, and reaction times. Characterization has to do with particle size, zeta potential, and oxidation reduction potential (pH and Eh).

The use of nZVI has major implications for solution pH and Eh. Preparations of nZVI also react with organic contaminants by hydrodechlorination. Lindane, a chlorinated pesticide, can also be degraded. Advanced nanomaterials, such as porous ZVI, have large surface areas, better hydraulics, high reactivity, and high mobility.

### ***Nano-ZVI versus Conventional ZVI: What Difference Does Size Make, Really?***

**Paul Tratnyek, Dept. of Environmental and Biomolecular Systems, OGI School of Science & Engineering, Oregon Health & Science Univ.**

Most current environmental remediation applications of nanotechnology involve particulate zerovalent metals, especially zerovalent iron (ZVI). Therefore, these applications have much in common with more-established applications of ZVI in remediation, such as “conventional” PRBs (Tratnyek et al. 2003). Since conventional PRBs are typically constructed with granular iron that is hundreds of micrometers to a few millimeters in size, it is widely assumed that the essential differences between conventional PRBs and remediation applications of nZVI stem from the high reactivity and mobility of nanosized particles.

With respect to mobility, it is now clear that movement of nZVI in environmental porous media will be very limited. Therefore, only two engineering scenarios seem realistic: (1) creation of “reactive treatment zones” by injection of nZVI in closely spaced wells such that the zones of injected material overlap and (2) source zone treatment by injection of nZVI in the immediate vicinity of NAPLs (Tratnyek and Johnson 2006). Engineering concepts that invoke movement of nZVI through porous media (groundwater or sediments) for more than a few tens of meters probably are misleading.

With respect to the reactivity of nZVI, there are several aspects. Due to a variety of “aging” processes, particle transformations are of practical as well as fundamental concern (Baer et al. 2007), but reactivity of the particles with contaminants has received the greatest attention. While many of the purported advantages of nZVI are predicated on it being more reactive than conventional, micro- to milli-meter sized ZVI, most studies on which this claim is based leave a host of potentially significant process variables uncontrolled or unresolved.

To obtain a more precise understanding of how the reactivity of nZVI differs from conventional ZVI, we performed a comparison of the properties of several nZVI preparations (Nurmi et al. 2005). The two types of nZVI studied most intensively included the original formulation of reactive nanoscale iron particles (RNIP-10DS) marketed by the Toda Americas Company (synthesized by high temperature reduction of goethite with H<sub>2</sub> and formulated and shipped as an aqueous slurry) and a sample provided by Dr. Wei-Xian Zhang prepared by the method used in early work at Lehigh University (reductive precipitation from a ferric chloride solution with borohydride). We designate these materials Fe<sup>H2</sup> and Fe<sup>BH</sup>, respectively.

Using carbon tetrachloride (CCl<sub>4</sub>) as a model contaminant, we found that while nZVI gives faster degradation rates on a mass-normalized basis, the surface-area-normalized rate constants for nZVI are about the same as conventional ZVI. Thus, we saw no evidence for a nanoscale effect on the “intrinsic” reactivity of ZVI over the range of conditions studied (Nurmi et al. 2005). We have confirmed that this conclusion applies quite broadly by extending the comparison of reaction rates with additional data from our laboratory and others (Tratnyek and Johnson 2006).

While the above concerns the effect of nZVI on rates of CCl<sub>4</sub> degradation, we are also interested in if there is an effect of nanoparticle size on the pathway or products of contaminant degradation. Our experiments show that Fe<sup>H2</sup> produces more favorable products (less chloroform, CHCl<sub>3</sub>) than Fe<sup>BH</sup> or conventional ZVI (Nurmi et al. 2005; Baer et al. 2007). Since the high yield of CHCl<sub>3</sub> obtained with conventional ZVI has been the main reason that ZVI is not widely used to remediate CCl<sub>4</sub>, the unusually low yield of CHCl<sub>3</sub> that we obtained with Fe<sup>H2</sup> may open up a new range of remedial options for CCl<sub>4</sub> contaminated sites.

Mining the literature for comparable data on CCl<sub>4</sub> reduction for other types of particles (Fe<sub>3</sub>O<sub>4</sub>, FeS, etc.) suggests that nanoparticles with a ZVI core do have higher reactivity than particles that do not contain ZVI. With other contaminants, nanoscale effects on kinetics and product distributions are quite different. For example, the explosives TNT and RDX apparently do exhibit a nanoscale effect on surface-area normalized rate constants, but no particle size effect on product distributions has been detected yet.

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***Transport of Modified Reactive Nanoscale Iron Particles in Subsurface Soils***  
**Krishna Reddy, Dept. of Civil & Materials Engineering, Univ. of Illinois at Chicago**

There are several types of environmental remediation research being conducted at the University of Illinois at Chicago, one of which is the use of nanotechnology for the characterization and remediation of contaminated soils, sediments, and groundwater. The focus of this particular research is based on the hypothesis that transport (delivery) of reactive nanoscale iron particles (RNIP) into a contaminated subsurface is essential for the success of this remediation technology. Some challenges associated with the research include: (1) RNIP cannot be transported through porous media without modifying their surface; (2) the subsurface environment is mostly heterogeneous and can be unsaturated and/or saturated, making the delivery of RNIP under such complex conditions challenging; and (3) there is no general reliable predictive model for assessing the transport of RNIP into the subsurface.

The five objectives of this research are to investigate: (1) transport of various surface-modified RNIP (MRNIP) in different saturated homogeneous porous media; (2) transport of MRNIP in different unsaturated and saturated heterogeneous subsurface environments; (3) enhanced transport strategies; (4) reactivity of nanoscale iron particles during their transport in different subsurface environments; and (5) transport and fate modeling of nanoscale iron particles.

The scope of the preliminary research includes a series of column experiments using four types of RNIP and natural silty sand. The four types of RNIP, provided by TODA America, Inc., are their original RNIP (10 DS) and three polymer coated MRNIP. Properties of the RNIP suspension are:  $\alpha$ -iron core and magnetite (iron oxide) shell composition; average particle size: 70 nanometers; 30 meters squared per gram of surface area; and 5,000 milligrams per kilogram sulfur content. The aqueous MRNIP slurry has a density of 1.20 grams per milliliter and is 17 percent solids.

The first step in the synthesis of RNIP (supplied by TODA America, Inc.) is acicular goethite (FeO(OH)), precipitated from oxygenated ferrous sulfate (FeSO<sub>4</sub>) solution. Next, the acicular goethite is reduced to  $\alpha$ -iron grains in a heated hydrogen gas atmosphere. The  $\alpha$ -iron grains are wet-milled, a process during which the surface converts to magnetite.

The procedure for this research involved loading the columns with soil to a height of 20 cm, injecting a slug of selected RNIP suspension at 2.0 grams per liter (g/L), flushing with deionized water or simulated groundwater, and analyzing effluent for pH, electrical conductivity (EC), total dissolved solids, and iron. Among the different polymer MRNIP, MRNIP-2 was found to transport relatively better under both deionized water (DI) and simulated groundwater (electrolyte) flushing. Using MRNIP-2, a series of enhanced transport strategies were then tested, including various polymer to RNIP ratios, different levels of pressure and conditions (pulsed and constant), and oxygen-free conditions (oxygen was replaced with nitrogen).

Preliminary results show that polymer MRNIP, specifically MRNIP-2, can be effectively transported through subsurface soils under pressurized conditions. Results also show that enhanced transport strategies must be investigated depending on the specific soil type and the surface modification of RNIP.

## Panel Session 2: Various Nanoparticles

### *Chemical and Biochemical Nanosensors Based on Single Wall Nanotube - Field Effect Transistor Devices*

**Erica Forzani, Dept. of Electrical Engineering & Center for Solid State Electronics Research, Arizona State Univ.**

The need for improved sensors is widespread, including the environment, security, health, industry, food quality, and more. The human body is the perfect sensor to emulate, in particular, neuronal synapses. Neuronal synapses are the perfect feed-back system to imitate because of their capability for recognition of elements, signal transduction, signal processing, and data communication. There is a need to miniaturize and integrate such an imitation and electrical detection is the method closest to the way neuronal synapses function.

Electrical detection allows for a high degree of integration for a miniaturized device to simultaneously detect different species. It also allows for simple processing, display, and transmittal of data and is compatible with microelectronics, enabling scientists to take advantage of existing microtechnology.

Field Effect Transistor (FET) nanosensors have many positive aspects. In a glucose sensor, there are no toxic mediators for transduction; they are 300 times faster and 100 times more sensitive than similar sensors on 20 micrometer ( $\mu\text{m}$ ) gap. Metal ion sensors are 500 times faster and  $4 \times 10^4$  times more sensitive. Nanoscale FET sensors are superior to microsensors because they can cross a gap smaller than 60 nm. In conventional sensors, such as FET, conduction through the channel region is two dimensional. In a one dimensional FET nanosensor however, sensitivity is enhanced because there are fewer pathways for charge carriers, less scattering, higher area to volume ratios, and a faster time response.

Single wall nanotubes (SWNTs) have unique structural and electrical properties. They are metallic and semiconducting. For a p-type semiconducting SWNT – FET, the “gate” and nanotube are like two plates in a capacitor. Carrier density can be changed by changing the gate potential (electrostatic induction) and negative backgate potentials can induce an increase of charge carriers (holes) in nanotubes (p-type semiconductor). P-type behavior is due to gold contact and adsorbed oxygen that acts as p-type dopant. Also, changing the chemical environment of a tube can change the doping level and lead to different sensor applications.

In order to convert a SWNT into a sensing element a method involving electropolymerization of peptide-functionalized monomers is used. This allows the peptides, composed of amino acids, to be used as molecular probes. Such probes can be used to detect such elements as copper in water or Hepatitis C by identifying a characteristic ribonucleic acid (RNA) sequence. Functionalizing SWNTs with peptide-polymers involves selectivity, sensitivity, conductance features, and versatility (the number of different peptide sequences is virtually unlimited). Real time detection of heavy metal ions and RNA sequences with extremely low detection limits has been demonstrated. Remaining issues of SWNT-FET sensors include: sample delivery (need for microfluidics), interconnection issues (going from nanoscale to macroscale world), avoiding the

effect of interference in complex matrix samples (non-specific binding), and detection restricted to electrical double layer length and contact versus wall side effects.

### **“Functionalized Nanoporous Ceramic Sorbents for Removal of Mercury & Other Contaminants”**

*Shas Mattigod, Applied Geology & Geochemistry, Pacific Northwest National Laboratory*

Nanoporous ceramic substrate has controlled pore channels 1.5-40 nm in diameter and a large surface area, ~600-1000 square meters per gram ( $m^2/g$ ). Self-assembled monolayers on mesoporous silica (SAMMS) have customized surface chemistry that can be designed to be extremely specific for adsorption of the target constituents. In addition to being very specific, the binding capacity and strength are very high. Thiol-activated SAMMS have been shown to be extremely effective at binding mercury, lead, and arsenic among other constituents.

Preliminary cost comparison shows SAMMS to be much more cost effective for mercury removal than resin or granular activated carbon (GAC). Additionally, in a performance analysis SAMMS adsorption was shown to not be affected by macro or trace cations, anions, or organics. The pH range was approximately 3-13. Loading was approximately 40 – 600 milligrams per gram (mg/g) with fast kinetics of around 99.9 percent at 5 minutes. A very high specificity was recorded at  $K_d$  of approximately 103 – 108 milliliter per gram (ml/g). Finally, SAMMS generates highly stable waste resulting in a low disposal cost.

Some applications for SAMMS include the purification of produced water, crude oil, smelter condensate, gas condensates, natural gas, and mustard gas. SAMMS are the next generation materials for hierarchical pore structured materials. Targeted applications include flue gas mercury removal, precious metal recovery, and sensors.

**SEPTEMBER 7, 2006**

## **Nanotechnology Life-Cycle Analysis**

### ***Industrial Ecology, Sustainability and Nanotechnology***

**Barbara Karn, EPA ORD-NCER and Woodrow Wilson International Center for Scholars,  
Emerging Nanotechnologies Project**

There is a research framework for nanotechnology and the environment that can be categorized by applications and implications. Applications address existing environmental problems or the prevention of future problems. Some applications are in the areas of green energy; treatment; remediation; sensors; and green nanotechnology. Implications, however, address the interactions of nanomaterials with the environment and any potential risks that may be posed by nanotechnology. Some areas of investigation under implications are toxicology; fate & transport and transformation; natural nanoparticle processes; exposure, bioavailability, and bioaccumulation; and life cycle aspects. Other areas of activity involving nanotechnology and the environment are standards development, international activities, regulatory and voluntary policies, state and local policies, public perception, risk-benefit analysis, and how the EPA might approach the nanotechnology, biotechnology, information technology, and cognitive science (NBIC) convergence.

The history of nanotechnology may be followed by reference to the following publications and conference proceedings:

- 1970 Industrial Ecology (magazine) published*
- 1972 Industrial Ecology in Japan*
- 1989 Frosch article in Scientific American*
- 1991 National Academy of Science colloquium*
- 1992 ATT Industrial Ecology Fellowships*
- 1992 National Academy of Engineering workshops*
- 1995 Graedel and Allenby textbook*
- 1997 Journal of Industrial Ecology*
- 1998 Gordon Research Conference*
- 2001 International Society for Industrial Ecology*

Industrial ecology is a rapidly growing field that systematically examines local, regional, and global materials and energy flows in products, processes, industrial sectors, and economies. It focuses on the potential role of industry in reducing environmental burdens throughout the product life cycle, from the extraction of raw materials to the production of goods, the use of those goods, and the management of the resulting wastes.

A system is a group of interacting, interrelated, or interdependent elements forming a complex whole. Industrial ecology takes a systems perspective by making a self-conscious attempt to avoid partial analyses (emphasis on a long-time horizon and global extent) and covering two bases for execution of systems-orientation, i.e., a life cycle view and materials balances. The scale of industrial ecology has three levels of operation: *macro* – understanding global and



national materials and energy flows; *meso* – industry studies and studies evaluating industrial symbiosis to understand regional and sector linkages; and *micro* – more local and specific studies such as design for environment (DfE), life cycle assessment (LCA), and pollution prevention (P2).

As reflected in the *Journal of Industrial Ecology*, industrial ecology topic areas include, but are not limited to, material and energy flows studies, dematerialization and decarbonization, technological change and the environment, and life cycle planning, design and assessment. Additional topic areas can also be found in the *Journal of Industrial Ecology*.

In most cases, there is no industrial materials cycle. If nanomaterials replace other materials, those other materials become the waste. Quantifying the metabolism of physical economies requires: total material requirement and output; physical input-output tables (PIOT); company-level materials/substance flow analysis (MFA); eco-balance, company materials accounting, and eco-audits; ecological footprint analysis; sustainable process index; life cycle assessment; material intensity per unit service; environmental space; substance flow analysis; and bulk internal flow MFA. Regarding industrial ecology tools and nanotechnology, beginning to look at processes and their impacts throughout the whole system is necessary. For example, there is growing use of over 60 new elements in the semiconductor industry such as the lanthanides and transition metals, each with currently unknown environmental impacts.

The circular economy involves closing loops in industrial systems. The Society of Environmental Toxicology and Chemistry (SETAC) definition for LCA states, “Life Cycle Assessment is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and materials used and releases to the environment; and to identify and evaluate opportunities to affect environmental improvements. The assessment includes the entire life cycle of the product, process or activity, encompassing, extracting and processing raw materials; manufacturing, transportation and distribution; use, re-use, maintenance; recycling, and final disposal” (SETAC, 1991). SETAC’s LCA steps include a flowchart, inventory emissions at each step, environmental effects, and a comparison of impacts.

LCA can evaluate overall material and energy efficiency of a system; identify pollution shifts between operations or media as well as other tradeoffs in materials, energy, and releases; and benchmark system efficiency improvements as well as reductions in releases. By itself, LCA cannot generate a comprehensive assessment of any system.

Eco-industrial parks (“industrial symbiosis”) can be depicted by the Kalundborg Model. Eco-efficiency revolves around activities that “Reduce, Reuse, and Recycle,” which leads to a reduction in resource depletion and destruction. It does not halt the process. Destruction takes place in smaller increments over a longer period of time. Product stewardship is a product-centered approach to environmental protection, also known as extended product responsibility (EPR), that calls on those involved in the product life cycle (i.e., manufacturers, retailers, users, and disposers) to share responsibility for reducing the environmental impacts of products. DfE is a systematic integration of environmental considerations into product and process design.

Green nanotechnology has two goals: producing nanomaterials and products without harming the environment or human health, and producing nanoproducts that provide solutions to our environmental changes. The Green Nanotechnology Framework involves production and products. Production of nanomaterials and products can be performed in a way that will not harm the environment. It is possible to make nanotechnology “greenly” (e.g.: green chemistry, green engineering, DfE, smart business practices) or use nanotechnology to “green” production (e.g., nanomembranes, nanoscaled catalysts, pollution prevention). Products of nanotechnology can help the environment through direct environmental applications (e.g., environmental remediation, sensors) or indirect environmental applications (e.g., to save energy and reduce waste). It is important to anticipate the full life cycle of nanomaterials and nanoproducts.

Nanotechnology is a very powerful new approach that will change our industries and our lives. We have a very small window right now to develop this technology prudently – to learn from past mistakes and concurrently look at the possibility of harmful implications as we increase the applications.

### **Risk Assessment of Nanotechnology**

#### ***A Proactive Approach to Nanotech EH&S***

**Aatish Salvi, Vice President, NanoBusiness Alliance**

When it comes to nanotechnology, there are some key messages to keep in mind. First, nanomaterials occur naturally in the environment. The use of new engineered nanomaterials can allow people the ability to better control the properties of these materials and has the potential to improve their performance over existing materials. People can be proactive in nanoscience by actively pursuing green nanotechnologies. Secondly, environmental health & safety (EH&S) research on nanomaterials suggests that society should be cautious. However, being alarmist damages the industry and public confidence. It is important to be proactive in consumer education by providing balanced perspectives for the media and public. Finally, the existing regulatory infrastructure has the authority and flexibility to handle nanotechnology without the need for new laws. It is possible to be proactive in policy by prioritizing the data gathering required for these regulations to intelligently adapt to the advances in nanotechnology.

It is also important to understand that nanomaterials are not new, as people have been unwittingly using nanomaterials for centuries to impart improved properties into materials. Nature made use of nanomaterials long before mankind learned how to leverage them. People have also been producing and dispersing “incidental” nanoparticles in tremendous volumes from hydrocarbon combustion for decades, possibly even centuries. However, the ability to control the properties that emerge from the deliberate synthesis of nanomaterials is largely new; rather than a serendipitous process of discovery, people are moving toward the rational design of materials.

As things approach the nanoscale, new properties emerge. These new properties can be “tuned” by control of the constituent composition, size, and spacing of materials. Specifically, nanotechnology will permit control of structural properties (e.g., strength and ductility), thermal

properties, catalytic properties, electrical properties, magnetic properties, and optical properties. This new degree of freedom changes and reduces the materials-related constraints engineers confront when designing products and allows new creativity in product design. It also allows companies to enhance commercially relevant properties while blunting biologically harmful ones.

There are many ways nanotechnology can lead to a greener tomorrow. Nanotechnology is on the forefront of air, water, and soil remediation; nanomaterials can replace known toxic materials in several applications; and nanomaterials can reduce pollution at its source by reducing consumption and enabling cleaner production.

It is important to look at both sides of the risk equation. While proceeding with caution is good, it is unnecessary to be alarmist. Some reasons for caution include: (1) the size of nanoparticles in some cases allows them greater mobility in organisms, soil, and water; (2) there is some evidence that indicates that inhalation of carbon nanotubes can cause lung inflammation; (3) intradermally injected nanoscale quantum dots were found to disperse into the skin and reach the lymph nodes; and (4) metrology and modeling for nanomaterials are still in their early stages and require improvements.

As previously stated, there is no need to be alarmist. The Center for Biological and Environmental Nanotechnology (CBEN) has found that water soluble carbon nanotubes are less toxic than their insoluble counterparts and that simple surface chemistry changes dramatically reduce the toxicity of carbon 60 (C60) and carbon nanotubes. Lawrence Berkeley Laboratory found that polyethylene glycol coated quantum dots can be absorbed into cells with minimal impact to cellular function at 1,000 times the dosage of typical use. Karlsruhe Research Center found that the type of salt used in toxicity tests can have major impacts on the toxicity of nanotubes due to the formation of crystals on the nanotube surfaces. Additionally, the workplace safety findings of the National Institute for Occupational Safety and Health (NIOSH) indicated that a “well designed exhaust ventilation system with high efficiency particulate air (HEPA) filters should effectively remove nanoparticles.”

A false, yet very public alarm can have detrimental effects on nanotechnology. Keeping a balance perspective is necessary. “Nanotechnology” is a brand with significant potential value, but it can be badly damaged and cause consumer confusion unless action is taken. The media plays a critical role in influencing consumer confidence and negative headlines are common. Even though most articles are balanced, 48 percent of the headlines about nanotechnology in the United States’ papers are negative. It is imperative to be proactive in providing a balanced perspective for the media and the public, and in protecting the use of the nanotechnology brand.

One major question of debate includes, “should new legislation be written specifically for nanotechnology?” The answer is, not until more research has been completed. There is already a regulatory framework in place. There are acts that regulate and manage materials and are thus regulating and managing nanomaterials under the auspice of materials. More research and understanding are needed before literature is created to manage and regulate nanotechnology specifically.

### **Panel Session 3: Nanotechnology Risks**

#### ***Environmental Transport, Fate, and Potential Risks of Nanomaterials***

**Greg Lowry, Dept. of Civil and Environmental Engineering, Carnegie Mellon Univ.**

The desired properties for functionalized nanoparticles for *in situ* remediation include stable dispersions, minimized filtration mechanisms, and nanoparticle-contaminant interaction. The risks associated with nanotechnology are largely unknown and are a function of both exposure and toxicity. It is thus necessary to monitor exposure pathways, fate and transport in the environment, and toxicity to determine actual risk.

Nanomaterial mobility in a porous material can be limited by aggregation, straining, attachment, and NAPL targeting. Factors affecting this mobility include chemical factors (pH, ionic strength, and surface chemistry) and physical factors (flow velocity, particle/aggregate size, heterogeneity). Nanoparticle aggregation in water can be attributed to high Hamaker constant, chemical bonding, hydrophobicity, and magnetic attraction. Small particles have high diffusion coefficients and thus experience many collisions between particles, leading to high aggregation rates. Nanoparticle aggregation can limit mobility. Attachment is also an important fate process as it limits mobility in porous material and may affect bioavailability/transformation/degradation. Attachment is a function of the particle type and coatings used. Surface modifiers can increase mobility by inhibiting aggregation and particle-media interactions. Mobility also depends highly on ionic strength and composition (divalent cations).

Are nanomaterials toxic? Many nanoparticles (e.g., fullerenes) are cytotoxic to diverse cell types and/or cause oxidative stress (OS). Toxicity is thought to be a function of size, surface area, surface charge, and functional groups. If inhaled or injected, particles can enter systemic circulation and enter various organs and tissues such as the liver, kidney, or brain. Additionally, nanoparticles can cross the blood-brain barrier and enter the central nervous system.

Research has shown that nanomaterials are predominantly present as aggregates, but (statistically) some single particles are also present. Nanoparticle mobility in porous media is low under typical groundwater conditions but surface modification can enhance mobility, even at high ionic strength and in the presence of divalent cations. Amphiphilic coatings offer the potential for targeting DNAPL and other types of modifiers offer potential for “targeted” delivery. Particles change with time through processes such as oxidation, hydroxylation, sorption to organic matter, and biotransformations. The type and fate of surface coatings used can greatly affect the potential for risk by modifying nanoparticle surface properties which can determine both their mobility (affecting exposure concentrations) and their toxicity.

#### ***Nanotoxicology and Industry***

**Shane Journey, Toxicology and Nanotechnology, Univ. of Saskatchewan**

‘Nano’ is now! Nanotechnology and nanoscale materials are already being used. Sunscreens use titanium dioxide and/or zinc oxide (TiO<sub>2</sub> and/or ZnO) nanoparticles, tennis balls are lined with ceramic nanoparticles, and pants are being embedded with nanowiskers for stain and

wrinkle resistance. Current nanomaterials include quantum dots (in medical electronics and diagnostic markers), nanotubes (being developed for a wide variety of applications ranging from composites to electronics and biomedical applications), nanosilicates (in paint pigments, tennis balls, and food packaging), and metal nanosilicates (in cosmetics and sunscreens). There are roughly 300 products on the market that claim to be improved via nanotechnology. With the growing application of nanotechnology to manufacturing processes and products, the human and environmental health aspects of this “disruptive” industrial technology will need to be addressed.

**Examples of Current Nanomaterials** - Carbon nanotubes are an example of high aspect ratio nanoparticles with two common examples being the single wall and multi-wall carbon nanotubes (SWNT and MWNT). SWNT are 1 - 2 nm in diameter and can be grown to more than one millimeter (mm) in length. MWNT have layered concentric walls and have diameters up to 20 nm, and can also be grown to be 1 mm in length. Nanotubes have a tensile strength approximately 100 times stronger than steel, yet they are a sixth the weight. They also have unique conductivity and molecular adsorption capacity. Buckeyballs or C<sub>60</sub> are being studied intensively for a variety of applications including drug delivery. Rosette nanotubes are another class of nanotubes (described below) which are free of metals and naturally water-soluble, which is in contrast to the SWNT and MWNT forms. At present SWNT, MWNT, and C<sub>60</sub> are the most studied engineered nanomaterials and are the most likely to be produced in commercial quantities in the future. Other current industrial or occupational health relevant nanoparticles include titanium dioxide, carbon black, and diesel exhaust particles.

**Why are Nanoparticles Different?** --- Nanoparticles (<100nm) have several characteristics that make them different from conventional materials. Examples of nanomaterial characteristics that are different because of their extremely small particle size (<100nm) include: much larger number of particles for a given mass dose; much larger surface areas (quantum effect); generally more reactive with higher surface energies; altered physicochemical properties; and resistance to dispersal. If nanoparticles did not have unique and different properties, we would not be so interested in applying them for new products and chemical processes.

These same properties which make nanoscale particles attractive also pose a challenge to the evaluation of their toxicity. Indeed, which dose-metric to use in toxicity studies (particle number, surface area, or mass) is still being debated and will likely be particle specific. Nanoscale particles may have altered toxicity due to binding or adsorption to other contaminants when exposed to different physiological environments in the body or when in contact with environmental systems or receptors. Until better methods for monitoring these nanoparticle properties in industrial environments is available, it is difficult to determine both the hazard and exposure components of the risk equation. Because the behavior of nanoscale particles in biological media and their fate and transport in organisms is just beginning to be understood, studies on the entire life cycle of nanomaterials are difficult at present. This is, however, an emerging key issue in industry. Future research efforts that will be a priority for industry will include understanding the lifecycle of nanoscale materials from raw materials production, handling, consumer use, disposal, and recycling phases of a product.

Understanding the properties of nanoscale materials which impart favorable or toxic responses is crucial to determining risk and controlling exposures in the industrial environment. Indeed, a

number of studies have examined the toxicity of SWNT from an occupational health standpoint. In contrast to SWNT, an organic class of nanotubes known as rosette nanotubes has a number of features which may impart biocompatibility. Characteristics of the helical rosette nanotube include: water solubility without modification; metal free synthesis (carbon, hydrogen, oxygen, and nitrogen); polydisperse length (shorter tubes of approximately 50-200nm are formed when synthesized at lower water temperatures while tubes can grow to a few microns at higher temperatures); a pH dependent aggregation state; and easy surface modification. This example highlights the possibility that, if some nanostructures have undesirable properties which may confer toxicity, it may be possible to “engineer out” such properties or “engineer in” biologically favorable characteristics. This of course can only be accomplished if the intended industrial or commercial property of the nanostructure is not compromised.

**Exposure** - Humans have been exposed to nanoparticles for hundreds of years ranging from sea salt to volcanic particulate and forest fire by-products. In the last 15 years a great deal of attention has been paid to the nanoscale or ultrafine (<100nm) component of particulate matter. Recently, the issue of possible exposures associated with scaled up production and handling of novel engineered nanomaterials has been raised.

Exposure to nanoparticles can result from cigarette smoke, diesel soot, tires, rubber products; welding smoke and exhaust, soldering, foundries, injection molding, grinding and polishing; nanoparticle based ceramics, paints, and cosmetics; quantum dots; and nanoparticle based medical products such as pharmaceuticals, drugs, and diagnostic agents. Unintentional exposures are particularly being focused on in industrial production and handling environments as related to occupational health. This is particularly important given that the traditional routes of exposure for occupational toxicants (inhalation and dermal) have unique considerations when studying the toxicological behavior and responses to nanoparticle exposure. Nanotoxicology will be discussed in detail in the subsequent presentation and certainly presents some novel issues for industry health and safety. Intentional exposure may occur from consumer products or medical applications. At present, adequate technology to precisely measure the toxicologically relevant components of nanoparticulate (particle number versus surface area versus mass versus volume) are in development and thus robust data on exposures is difficult to ascertain at present.

Present day activity for manufacturing and use of nanomaterials is 49 percent in the United States, 30 percent in the European Union, and 21 percent in other parts of the world. The emphasis of the nanomaterial manufacturing industry in the United Kingdom has been bulk markets in metals and metal oxides, as well as some niche markets such as quantum dots, and does not reflect the global emphasis on fullerenes, nanotubes, and nanofibers. The manufacturing of nanoscale metals, polymers, silica, clays, and ceramics represent mature processes capable of generating large commercial quantities of materials (*Aitken et al. Occup Med 56:300-06; 2006*).

Nanomaterial safety considerations in research and development environments are of great interest to industry at present. Through voluntary reporting schemes, submission of any procedures or data regarding health and environmental effects from products using nanotechnology are encouraged. This is presently being attempted in the United Kingdom.

**Summary** - Nanomaterials have novel properties that deserve consideration. At present, there is still need for data on both the toxicity of nanomaterials and techniques to adequately assess exposures to nanomaterials. Life cycle analysis will be very important as the science continues to develop. Further understanding of nanoparticle interaction with other contaminants and organisms in the environment is required and case studies of industrial operations are needed. As the science of nanotechnology, nanotoxicity testing, and nano-exposure assessment matures, there will be a need for education and training of appropriate personnel to ensure the responsible growth of the nanotechnology industry.

### **“Risk Assessment of Nanoscale Metal Particles”**

*Joyce Tsuji & Fiona Mowat, Exponent, Health Services Practice*

The Nanotechnology Consumer Products Inventory lists 212 products from more than 15 countries (60 percent of which are manufactured by the United States). The largest categories are health and fitness (i.e., sporting goods, cosmetics, sunscreens), electronics and computers, and home and garden.

The Risk Assessment Framework begins with hazard identification (including chemical composition, particle size, structure, properties, coatings); moves to exposure assessment (dispersed or aggregate, coatings integrity, receptor, entry routes) and toxicity assessment (uptake, distribution, metabolism, excretion, reactivity, dosimetry); and ends with risk characterization (likelihood of effects, affected population, type of effects).

Nanoscale metal particles include pigments, zerovalent metals, and metals used in therapeutics, electronics, and aerosols. Key exposure issues for human health and the environment are defined by the degree of containment or encapsulation, environmental fate and transport, availability of technology to conduct relevant exposure measures, and effectiveness of current approaches for occupational and consumer protection. There are no agreed upon methods for measuring airborne nanoscale exposures. Options include a mass-based approach, size distribution, number concentration, and surface area. The best method may vary with the nanoparticle, for example, the NIOSH Current Intelligence Bulletin on titanium dioxide (TiO<sub>2</sub>) suggests that particle surface area is the better dose metric for TiO<sub>2</sub> than mass or number.

Materials science analysis includes performance (i.e., durable, encapsulated, stable), properties (i.e., toughness, adhesion, friability, environmental resistance, diffusion rates), structure (i.e., polarity, crystallinity, reactivity), and process (i.e., mixing, heating, application). Exposure potential is influenced by coatings durability, product integrity, properties of the particles themselves and that of the binders used. Encapsulation limits exposure when nano-iron is incorporated in resin beads. They have high effective capacity (rapid absorption, tight binding, and high equilibrium capacity) and regeneration is possible so that they can be reused multiple times and their use results in a relatively small volume of solid waste.

The good news is there is substantial awareness of the issue; processes are “similar” to other chemical production processes; current personal protection measures are likely adequate;

airborne materials may quickly agglomerate while dispersing; filtration is probably effective for airborne nanoparticles; and exposure might actually be quite low.

For people involved in manufacturing or synthesizing nanoparticles, it is recommended that the work area be well ventilated and the product be mixed within enclosed vessels or in liquid slurry; that nanoparticles be encapsulated to prevent release; and that “best practices” and standard operating procedures be evaluated. Exposure of any new product, as well as older products, should be evaluated and “lessons learned” from other materials should be used when applicable, as well as performance of exposure potential analyses. Toxicology issues for nanoparticles include their ability to cross biological barriers, such as cell membranes, skin, and lungs and their higher reactivity from their relatively large surface area.

Zerovalent iron nanoparticles are novel nanoproducts that can reach cells. Their lack of charge may allow more nZVI to enter cells more freely, but there has been little research on the effects. Passage of nanoparticles through red blood cell membranes is size dependent, rather than surface charge or particle type dependent. The effects of particle size on pulmonary inflammation show toxicity depends on surface area rather than mass. Direct transport to the brain via sensory neurons has been demonstrated via deposition and translocation of inhaled particles.

Dermal studies, mostly involving TiO<sub>2</sub> and zinc oxide used in sunscreens, show photoreactivity can be mitigated by surface coatings. Also, there is little evidence of penetration to living layers for unbroken skin; however, penetration via follicles or areas of flexion is possible. Research by the National Toxicology Program (NTP) and Food and Drug Administration (FDA) to evaluate penetration using quantum dots is ongoing.

Ecological toxicology shows ecological risk is based on particle stability and short-term toxicity of fullerenes to fish, daphnia, and bacteria. Nanometal oxides have anti-microbial effects and nano-ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) is more cytotoxic *in vitro* than ferrous iron.

Standard screening tests of relative toxicity of engineered nanoparticles are being developed and ecotoxicity testing should be considered in order to comply with existing performance-based limits which regulate discharges. Both short-term and long-term tests should be conducted.

#### **Panel Session 4: Human Health Impacts**

##### ***Pharmacokinetics, Tissue Distribution, and Excretion of Polyacrylamide Nanoparticles*** ***Yvan Wenger, School of Public Health, Univ. of Michigan***

Polyacrylamide (PAA) nanoparticles are neutrals, polymeric, and approximately 60 nm in diameter. Their applications range from controlled drug delivery to molecular targeting to photodynamic therapy to Magnetic Resonance Imaging (MRI) contrast agent. Certain modifications lead to specific changes in PAA properties, such as a polyethylene glycol (PEG) coating leads to increased blood circulation time and a biodegradable cross-linker enhances degradation.



Health impacts of PAA nanoparticles were evaluated by investigating the pharmacokinetics. In rats, after a single intravenous administration of up to 500 milligrams per kilogram (mg/kg), no visible damage to the rat tissues was observed. Excretion was found to be proportional to blood concentration and blood concentration exhibited three distinct behaviors: Phase I consisted of rapid distribution to organs; Phase II consisted of distribution throughout the body (0.5 - 27 hrs); and Phase III during which excretion occurred (0.5 - 340 hrs). The long half-life of PAA suggests that accumulation in the body is possible with repeated dosing.

### ***Life Cycle Assessment of Nanotechnology-based Remedial Technologies***

**Olivier Jolliet, Dept. of Environmental Health Sciences, Univ. of Michigan**

The need to provide quantified analytical tools to evaluate different kinds of materials, in order to go beyond "a priori", can be illustrated by the following example in which the environmental impact of polystyrene packing filler is used versus popcorn. Since polystyrene chips used for packing filler are made with a non-renewable raw material (petroleum) and are not biodegradable, popcorn has been proposed as a substitute material both because it is a renewable resource and it is biodegradable.

Jolliet et al. (1994) showed that, for each unit of mass of material, popcorn is three to four times more favorable than polystyrene. However, popcorn is 4.6 times denser than polystyrene chips. Therefore, popcorn is equal or worse than polystyrene if impacts are calculated per functional unit, i.e., per unit volume of packing filler. Consequently, the relative density of packing filler material is the key parameter from the environmental point of view. Thus, more environmental gain could be achieved through decreasing the popcorn density by as much as 46% rather than reducing the quantity of fertilizer used to grow the popcorn or of water used to wash the popcorn.

Counter to intuition, popcorn environmental friendliness was successfully enhanced beyond that of polystyrene via increased industrial processing, i.e., by extracting the starch from the popcorn and decreasing its density by about 46% via blowing it much like the polystyrene (Dinkel et al., 1996). Initially, the result is astonishing and paradoxical: a more industrially processed and therefore less near to nature popcorn will be more favorable to the environment than unprocessed popcorn. This example illustrates that the intuitive concept of "natural" does not necessarily correspond to the one of "environmentally friendly". Also, this example shows that the environmental benefit from a biomaterial is directly linked to its functionality in the context of a given application. It is therefore not possible to discuss the benefits of a material or of a remediation technique only according to its intrinsic characteristics. The popcorn case shows the potential synergy between technological optimization (in this case, the reduction of weight and quantity of material used) and energetic and environmental optimization.

Remediation of a contaminated site in Bioley-Orjulaz, Switzerland led to a comparison of risks and impacts of six remediation scenarios. The old municipal Swiss landfill was contaminated with 5 m<sup>3</sup> of polycyclic aromatic hydrocarbons (PAH) in the form of 3,600 m<sup>3</sup> of highly polluted soil and 5,400 m<sup>3</sup> of nominally polluted soil. The involved parties wanted to discern the environmentally friendliest technology to use for remediation. The key parameters were identified and trade-offs between the six alternatives were compared and assessed. Modeling of

contaminant fate and exposure pathways demonstrated that the key parameters depended on the amount, fate, and effects of hazardous air pollutants (HAPs). Contaminant mass in the environment was characterized by transfer fractions and contaminant residence times and human intake was characterized by bioaccumulation factors and ingestion rates. Contaminated soil transportation and the capacity to generate electricity were key factors in the results. It was concluded that incineration in a cement plant was the best alternative for the highly contaminated soil whereas burial in a landfill was the best alternative for the inert materials and the nominally contaminated soils. Soil washing and biological treatment were eliminated due to the abundance of fine particles and degradation resistant contaminants.

Initially, the application of LCA to nano-based remedial technologies would perhaps need to consider the same factors needed for conventional LCA as described in the Bioley-Orjulaz site example. It would require the consideration of the following key issues and data calculated on a function basis: transportation impacts; energy and material inputs for each treatment option; detailed data on nanomaterial manufacturing and the quantity produced; direct emissions of toxic substances released during treatment with nanoproducts; direct emissions of toxic nanomaterials, either the nanomaterials initially used or those produced by interaction with the toxic materials that are being treated; and data on partitioning properties, intake fraction, and dose-response levels.

In order to use known LCA methods certain unique nano-specific questions must be answered. For instance:

1. How may one identify the life cycle risks of new nano-based products and materials compared to conventional products?
2. What are the emissions associated with nanomaterial manufacture and processing compared to those of conventional products?
3. What are the mechanisms affecting fate and biological effects of nanoparticles?

We have developed an extended life cycle framework to analyze the trade-offs between risks to human health and benefits of nanotechnologies as a replacement for conventional technologies. First, a matrix approach has been developed to identify the main risks associated with nanotechnologies over the whole product life cycle (raw material extraction, manufacturing, use, disposal, and recycling). The matrix approach compares the additional human health risks with the benefits directly due to nanotechnologies. Also, indirect risks and impacts of nanotechnologies are compared to risks that are avoided by the use of conventional technologies. For each case, key factors of influence are identified.

Secondly, a comparative risk model has been developed combining a multi-media model with pharmacokinetic modeling of nanoparticle behavior. Based upon this framework, a comparison of potential benefits and risks of nanotechnology-based remedial technologies are analyzed.

Consideration of the analysis results provided by this extended model suggests that the choice of remediation techniques is a trade-off between transportation, treatment energy, and direct impacts of remediated toxicants and the nanomaterials used to remove or make them unavailable. The developed life cycle framework is able to assess risks of nanotechnologies in comparative approaches. However, the heterogeneity of compounds and processes involved require that

specific nanoscale characteristics be determined and it is imperative that corresponding databases to store such information are created. Once extended, the life cycle analysis framework is appropriate to analyze the trade-offs between remedial techniques based on nanomaterials versus conventional materials.

***Functional Optical Polymer Nanoparticles: Uses and Toxicology***

**Martin Philbert, Sr. Assoc. Dean for Research, School of Public Health, Univ. of Michigan**

Nanomaterials are here. “Nano” is far from a monolithic approach; the chemistry, physics, and material science aspects of nanotechnology allow for smaller, brighter, faster components as well as novel physical properties below 100 nm. Nanotechnology also allows for bottom-up construction, formulation of molecular assemblies, and ultimately, control. Existing nanotechniques include electro-wetting, optical fibers, dendrimers, liposomes, nanoporous materials, and macromaterials composed of aspect ratio fibers.

Probes encapsulated by biologically localized embedding (PEBBLEs) may be synthesized with diameters in the range 20-60 nm. PEBBLEs protect dye from cellular artifacts and also protect the cellular environment from dye toxicity. PEBBLEs allow for physical and chemical quality control of size distribution, detergent content, oxygen yield, photobleaching, pH stability, non-specific protein binding, leaching tests, colloidal stability, dye labeling efficiency, and magnetic potency.

Matrices include hydrophobic materials (e.g., plasticized polyvinyl chloride (PVC) and polydecylmethacrylate); hydrophilic materials (e.g., polyacrylamide-hydrogel); and amphiphilic materials (e.g., sol-gel and ormasil). Sensors are prepared as a result of polymer matrix and synthesis techniques, either micro-emulsion or a modified Stöber method.

Examples of uses include optical imaging of nitric oxide in living cells, quantitative intracellular nitric oxide measurements, and intracellular 3-D registration of sensors. Other applications include the detection of small molecules and ions and the measurement of electric fields in cells.

In 1906, Einstein formulated the theory of Brownian rotational diffusion. This rotation has now been visualized with a single nanoparticle, prepared by a combination of physical and chemical nanofabrication processes. Miniaturization reduces observation time from days to seconds and allows for determination of viscosity, temperature, and/or magnetic fields.

## **Attachment 1: Nanotechnology for Site Remediation Workshop Agenda**

# AGENDA

NANOTECHNOLOGY FOR SITE REMEDIATION WORKSHOP  
U.S. EPA Region 5, September 6-7, 2006

## DAY 1

<u>Time</u>	<u>Subject</u>	<u>Speaker</u>
8:30 - 9:00	Registration	
9:00 - 9:05	Introduction and Overview	Charles Maurice & Warren Layne
9:05 - 9:15	Welcome and Opening Thoughts	Rick Karl
9:15 - 10:10	Introduction to Nanotechnology for Site Remediation	Wei-Xian Zhang
10:10 - 10:40	Worldwide Nanotechnology Status	Barbara Karn
10:40 - 10:50	Break	
10:50 - 11:20	Cases of Nanotechnology Use at Superfund Sites	Martha Otto
11:20 - 12:00	Site Remediation Case Study	Mary Logan
12:00 - 1:00	Lunch on own	
1:00 - 2:15	Panel Session 1: Zerovalent Iron Nanoparticles	Wei-Xian Zhang Paul Tratnyek Krishna Reddy
2:15 - 2:45	Panel Discussion 1: Site Remediation	All
2:45 - 2:55	Break	
2:55 - 4:10	Panel Session 2: Various Nanoparticles	Erica Forzani Shas Mattigod
4:10 - 4:40	Panel Discussion 2: Site Remediation (cont'd.)	All

# AGENDA

NANOTECHNOLOGY FOR SITE REMEDIATION WORKSHOP  
U.S. EPA Region 5, September 6-7, 2006

## DAY 2

<u>Time</u>	<u>Subject</u>	<u>Speaker</u>
9:00 - 9:15	Welcome/Brief Day 1 Recap	Charles Maurice
9:15 - 10:00	Nanotechnology Life-Cycle Analysis	Barbara Karn
10:00 - 10:15	Break	
10:15 - 11:00	Risk Assessment of Nanotechnology	Aatish Salvi
11:00 - 11:30	Poster Presentations	
11:30 - 12:30	Lunch on own	
12:30 - 2:00	Panel Session 3: Nanotechnology Risks	Greg Lowry Shane Journeay Joyce Tsuji Fionna Mowat
2:00 - 2:30	Panel Discussion 3: Nanotechnology Risks	All
2:30 - 2:40	Break	
2:40 - 4:10	Panel Session 4: Human Health Impacts	Yvan Wenger Oliver Jolliet Martin Philbert
4:10 - 4:40	Panel Discussion 4: Nanotechnology Risks (cont'd)	All

## **Attachment 2: Speaker Biographies**

## Speaker Biographies

### **Erica Forzani**

Erica Forzani is an Assistant Research Professor in the Department of Electrical Engineering at Arizona State University (ASU) in Tempe, Arizona. She joined ASU in 2003 as research associate in N.J. Tao's group after receiving her Ph.D. in chemistry in 1999 from Cordoba National University, Argentina and holding a post doctoral position at the University of Buenos Aires, Argentina from 2000 to 2003. For the past few years, she has been working on the development of nanosensors for chemical and biochemical detection of environmental and health care analytes, using different methods based on optical, electrical, and acoustic detection. Her current research interest is the analytical performance optimization of new liquid and gas phase detection sensing devices.

### **Olivier Jolliet**

Olivier Jolliet is an Associate Professor in Environmental Health Science at the University of Michigan, Ann Arbor and is one of the founding members of the Center for Risk Science and Communication. His research and teaching programs aim to assess environmental risks and impacts of chemicals and innovative technologies in order to 1) assess the life cycle risks, impacts, and benefits related to new technologies (e.g., nanotechnologies, telecommunication systems) and materials in order to prevent emissions and guide the development of these technologies; 2) develop a flexible risk assessment framework, enabling specialists to contribute to an interdisciplinary comparative approach from chemical emissions to risks and impacts; and 3) model population-based exposure, intake fractions, and pharmacokinetics for outdoor and indoor chemical emissions in a consistent way.

He co-initiated the UNEP/SETAC (United Nations Environment Program / Society of Environmental Toxicology and Chemistry) Life Cycle Initiative and is the scientific manager of its Life Cycle Impact Assessment program. Olivier Jolliet obtained M.S. and Ph.D. degrees in building physics, the latter in 1988 from the Swiss Federal Institute of Technology at Lausanne (EPFL). He held a postdoctoral position at the Silsoe Research Institute (England) and was a visiting scholar at both the Massachusetts Institute of Technology (MIT) and University of California at Berkeley. Between 1999 and 2005, he was an assistant professor at the EPFL in Switzerland, where he headed the Industrial Ecology & Life Cycle Systems Group. In 2005, Olivier Jolliet was appointed an Associate Professor with tenure at the University of Michigan.

### **Shane Journey**

Originally from Liverpool, Nova Scotia, Canada, Shane Journey completed his B.S. and M.S. degrees at the University of Ottawa. His masters degree focused on human cardiovascular and thermoregulatory control. He has an active interest in human health and performance physiology in extreme environments. Shane has worked extensively in the area of industrial soft tissue injuries in both Canada and the United States. Specifically he has been employed with Human



Performance Systems (Waterville, Maine) and was involved in industrial ergonomic analysis, as well as in the prevention and treatment of accumulation trauma injuries. He has also completed research as an ergonomics & environmental health and safety specialist with Nortel Networks. Shane is currently finishing his Ph.D. thesis in toxicology and nanotechnology at the University of Saskatchewan. His research has been funded by awards from the Natural Sciences and Engineering Research Council of Canada and the Canadian Institutes of Health Research to study the toxicology and biocompatibility of nanomaterials. He is interested in both the occupational and environmental health aspects of nanotechnology as well the therapeutic potential of nanomedicine. Shane has given many invited talks on nanotechnology and its relevance to human and environmental health and recently represented Canada at the International Space University summer session program in Strasbourg, France, where he completed an international team project on micro and nanotechnologies in the space industry.

### **Warren Layne**

He has a BA in Chemistry from Boston University, MS in Inorganic Analytical Chemistry from University of Massachusetts, and Ph.D. in Medicinal Chemistry from Northeastern University in Boston, with postdoctoral training at Harvard School of Public Health in Nuclear Medicine. He also has years of industrial experience in Radiopharmaceutical research and has been an Assistant Professor at University of Connecticut Medical Center, University of Texas at Galveston and Baylor University in Houston, Texas.

Dr. Layne has spent 16 years at the Environmental Protection Agency, 11 years as Toxic Release Inventory Coordinator in Dallas, Texas (Region 6) in the Pollution Prevention and Toxics Division and 5 years as a Quality Assurance Plan Reviewer, Regional Sample Coordinator, and 2 years as the Nanotechnology Expert for Chicago, Illinois (Region 5) in the Superfund Division.

He was a coauthor of *Nanotechnology White Paper*, participated in EPA-sponsored National Nanotechnology Conferences and presented talks on Nanotechnology in various venues.

### **Mary Logan**

Ms. Logan is an experienced Remedial Project Manager (RPM) in the Superfund Division at the EPA Region 5 offices (Chicago). Ms. Logan joined EPA in 1985 in the Resource Conservation and Recovery Act (RCRA) permitting program. In 1988, she transferred to the Superfund program. From 1992 until 2004, Ms. Logan worked in the Superfund program at the EPA Region 2 offices (New York City). She works on large and complex Superfund sites and primarily has worked on sites with an enforcement component. Ms. Logan has worked with both federal agency and private responsible parties. Ms. Logan frequently serves as an instructor for a variety of environmental topics. She has also frequently presented or moderated at conferences, especially related to sediment issues. Prior to joining the EPA, Ms. Logan worked in research laboratories. Ms. Logan received her M.S. in environmental and occupational health sciences from the School of Public Health at the University of Illinois at Chicago and her B.A. in biology from the University of Chicago.

### **Greg Lowry**

Gregory V. Lowry is an Associate Professor in the Department of Civil and Environmental Engineering, and has been at Carnegie Mellon University since 2001. He received his B.S. in chemical engineering from the University of California at Davis, his M.S. in civil and environmental engineering from the University of Wisconsin at Madison, and his Ph.D. in civil and environmental engineering from Stanford University. His general area of research is environmental nanotechnologies including nanoparticle characterization, elucidating the reactions they promote, and their fate, transport, and toxicity in the environment. Dr. Lowry's research group currently investigates the use of novel surface coatings to enhance the mobility of zerovalent iron and metal oxide nanoparticles used in the subsurface for aquifer restoration and that promote adsorption of nanoparticles to the contaminant-water interface. Dr. Lowry also has projects on sediment remediation and contaminant transport in porous media, including developing and evaluating "active" sediment caps that destroy and/or sequester PCBs and several projects on carbon sequestration.

### **Shas Mattigod**

Dr. Mattigod has a B.S. in Civil Engineering from University of Mysore, an M.S. in Civil Engineering from University of New Hampshire and a Ph. D. in Environmental Chemistry from Washington State University and research at Pacific Northwest National Laboratories for the last eight years. His interests include Characterizing and developing radiation methods for liquid and solid effluents, leachates, RCRA wastes, contaminated soil, and groundwater from CERCLA Sites, Environmental Chemistry and Project Management. He is currently concentrated on the preparation and testing of functionalized nanoporous ceramic sorbents for the removal of at least 30 inorganic contaminants from contaminated sites.

### **Charles Maurice**

Since April 2004, Chuck Maurice has served as the EPA Office of Research and Development (ORD) Superfund & Technology Liaison (STL) to Region 5. As such, he holds a joint appointment with the Office of Science Policy in ORD and with the Innovative Systems & Technology Branch in the Region 5 Superfund Division. Chuck provides technical support regarding hazardous substances both through his own expertise as an ecological risk assessor and by coordinating with other scientists in the technical support centers and laboratories throughout ORD. He also communicates Regional research priorities and needs to ORD.

From 1995 to 2004, Chuck was an ecologist and ecological risk assessor the Region 5 Office of Strategic Environmental Analysis (OSEA), both in the immediate office and on the Critical Ecosystems Team. Chuck was an ecological risk expert, corrective action manager, and permit writer in the RCRA Permitting Branch, Region 5 Waste Management Division from 1993 to 1995. Before coming to EPA, Chuck was a senior ecologist and ecological risk assessor for the Superfund contractor Ecology & Environment, Inc. Chuck holds a B.S. degree (1980) in environmental biology from Eastern Illinois University, a M.S. degree (1982) in biological sciences from Bowling Green State University, and a Ph.D. (1989) in plant biology from the University of Illinois at Urbana-Champaign.

### **Fionna Mowat**

Fionna Mowat, Ph.D., is a Senior Managing Scientist with Exponent's Health Sciences practice. She is experienced in human health and ecological risk assessment and is trained in biomedical engineering. Her primary focus is conducting exposure assessments of various chemicals, mineral fibers, and nanomaterials in occupational settings and consumer products. She has presented several papers on nanomaterials at conferences and, with Dr. Tsuji, is a co-chair of the 2007 carbon nanotube workshop. Most recently, she presented a review of nanotechnologies used in the water market with discussion of their potential benefits and risks to human health and the environment, at the National Standards and Technology Institute of Nanotechnology Conference.

### **Martin Philbert**

Martin Philbert received his Ph.D. in 1988 in neurochemistry and experimental neuropathology from the Royal Postgraduate Medical School of London University in England. There he received a Medical Research Council Scholarship in experimental neuropathology. In the spring of 1988, Dr. Philbert was recruited as postdoctoral fellow in neurotoxicology at Rutgers University. While at Rutgers, Dr. Philbert investigated mechanisms by which chemicals that gain access to the central nervous system produce specific neurotoxic effects. In 1995, he joined the Toxicology Faculty at the University of Michigan as an assistant professor. Dr. Philbert is a Professor of Toxicology and Senior Associate Dean for Research at the University of Michigan, School of Public Health. He has provided service on a variety of committees at the University including the President's Commission on Undergraduate Education, University Taskforce on Multidisciplinary Teaching, and the University Committee on the Use and Care of Animals. Currently, Dr. Philbert provides consultation to the National Cancer Institute, National Institute of Environmental Health Sciences, National Toxicology Program, and Board of Scientific Counselors of the EPA and he is a scientific advisor to the International Life Sciences Institute in Washington, D.C. He teaches courses in general pathology, toxicological pathology, and mechanisms of neurotoxicity. Dr. Philbert's research interests include the development of nanotechnology for intracellular measurement of biochemicals and ions and for the early detection and treatment of brain tumors. He is also actively engaged in the investigation of mechanisms of chemically-induced energy deprivation syndromes in the central nervous system. He has published more than 100 scholarly manuscripts, book chapters, and abstracts and is the recipient of the 2001 Society of Toxicology Achievement Award. Dr. Philbert holds or has held grant awards from the National Cancer Institute, National Institute of Environmental Health Sciences, DOD - Defense Advanced Research Projects Administration (DARPA), EPA, and W.M. Keck Foundation.

### **Joyce Tsuji**

Joyce Tsuji, Ph.D., DABT, is a Principal with Exponent's Health Sciences practice and is a board-certified toxicologist with 19 years of experience in toxicology and risk assessment. Her particular areas of interest include exposure assessment and toxicology of a variety of chemicals, including those from industrial releases and in consumer products. Dr. Tsuji has directed several projects to survey the available literature and assess potential exposure and risks of specific

nanosized materials used in consumer products. She also organized and chaired a symposium on health risks of nanomaterials at the Society of Toxicology (SOT) Annual Meeting in 2005 and published the proceedings. Dr. Tsuji has presented at multiple conferences on applications and risk assessment of nanomaterials and has recently organized a workshop on health risk assessment of carbon nanotubes for the 2007 SOT Annual Meeting.

### **Paul Tratnyek**

Paul G. Tratnyek is currently Professor in the Department of Environmental Science and Engineering at the OGI School of Science & Engineering of the Oregon Health & Science University (Portland, OR). He received his Ph.D. in applied chemistry from the Colorado School of Mines in 1987; served as a National Research Council Postdoctoral Fellow at the EPA laboratory in Athens, Georgia, during 1988; and as a Research Associate at the Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG) from 1989 to 1991. His research addresses the pathways, kinetics, mechanisms, and other fundamental, molecular aspects of the reactivity of organic substances in the geochemical environment. Since 1992, Dr. Tratnyek has led research on the chemistry of permeable reactive barriers containing zerovalent iron (<http://cgr.ebs.ogi.edu/iron>). He co-organized the first symposium on contaminant remediation with zerovalent metals (Anaheim, CA, April 1995) and the first major symposium on the environmental fate of fuel oxygenates such as MTBE (San Francisco, CA, April 1997). Related information is available at <http://www.ebs.ogi.edu/tratnyek/>.

### **Yvan Wenger**

Yvan Wenger obtained a B.S. degree in biochemistry in 2003 at the University of Geneva and an M.S. degree in natural environmental sciences from both the Universities of Geneva and Lausanne. As a part of his masters thesis, he spent one year at the Swiss Federal Institute of Technology in Lausanne (EPFL) specializing in modeling techniques such as mass balance modeling. Since September 2005, he has been pursuing a doctoral degree involving nanoparticles modeling at the School of Public Health, University of Michigan.

### **Krishna R. Reddy**

Dr. Krishna Reddy is a Professor of Civil and Environmental Engineering at the University of Illinois at Chicago (UIC). Dr. Reddy received his Ph.D. from the Illinois Institute of Technology, Chicago. He received gold medals for being first in his class of B.S. students in civil engineering at the Osmania University and M.S. students in geotechnology at the Indian Institute of Technology in Roorkee. Dr. Reddy is a professional engineer in the State of Illinois and he worked as a civil engineer and project manager in consulting engineering companies for several years prior to joining the UIC. Dr. Reddy's consulting and research expertise includes geotechnical engineering, remediation of contaminated sites, waste containment systems, and waste material characterization and reuse. Dr. Reddy has published over 150 technical papers on various topics in geotechnical and geoenvironmental engineering. He is also the author of the book *Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies* published by John Wiley. Dr. Reddy is Editor of the journal

*Land Contamination & Reclamation* and he serves on the editorial boards of the *Journal of Soil and Sediment Contamination*, *Journal of Geotechnical and Geoenvironmental Engineering*, and *Journal of Hazardous Materials*. He has received several awards and honors for excellence in teaching, research, and professional service. See [www.uic.edu/~kreddy](http://www.uic.edu/~kreddy) for more information.

### **Barbara Karn**

Barbara Karn is an environmental scientist at the EPA. She recently returned from a detail to the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars. Her focus is “green” nanotechnologies - including using green chemistry, green engineering, and environmentally benign manufacturing to make new nanomaterials and products or using nanotechnology to prevent pollution in current processes. Nanotechnology is new enough that there is a huge opportunity to get it as environmentally right as possible. Dr. Karn has managed portfolios of research grants programs for pollution prevention technologies and nanotechnologies at the EPA Office of Research and Development. She holds a Ph.D. from Florida International University in marine ecology with emphasis on kinetics of nutrient cycling and a B.S. degree in chemistry from the Ohio State University. Dr. Karn has worked in industry, academia, and government. Her professional background ranges from electroplating to polymers, from environmental consulting to small business owner, and from academic administrator to water quality management planner.

## **Attachment 3: Participant List**

## Participant List

Last Name	First Name	Title	Company/ Affiliation	Address 1	City	State	Zip Code	Phone Number
Adler	Kevin	Environmental Scientist	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-7078
Ahmed	Syed	RPM	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-4445
Ascada	Yuki	General Manager	Toda America Incorporated	1920 North Thoreau Dr., Suite 110	Schaumburg	IL	60173	(847) 397-7060
Austrins	Leanne	Hydrogeologist	CH2M Hill	4287 s Reindeer Ct	Gilbert	AZ	85297	(480) 279-1130
Aycock	Mary	RPM	US EPA, Region 9	75 Hawthorne Street	San Francisco	CA	94105	(415) 972-3289
Ballard	Wm. Turpin	RPM	US EPA, Region 4	61 Forsyth St.	Atlanta	GA	30075	(404) 562-8553
Berman	Laurel	Brownfields Coordinator	Agency for Toxic Substances and Disease Registry (ATSDR)	77 West Jackson Blvd. Suite 413	Chicago	IL	60604	(312) 886-7476
Bickmore	Clint	VP Manufacturing	OnMaterials	629 Bross St.	Longmont	CO	80501	(303) 952-4520
Black	Christopher	Geologist	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-1451
Boice	Richard	Environmental Engineer	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-4740
Bolio	William	Geologist	State of Michigan - Department of Environmental Quality	Constiution Hall, 3rd Floor, South West Allegan Street	Lansing	MI	48909	(517) 373-9828
Brauner	David	Ecologist	US EPA, Region 5	77 W. Jackson Blvd	Chicago	IL	60604	(312) 886-1526
Bruck	Glenn	Hyrdogeologist	US EPA, Region 9	75 Hawthorne St.	San Francisco	CA	94015	(415) 972-3060
Caine	Howard	RPM	US EPA, Region 5	77 W. Jackson Blvd.	Chicago	IL	60604	(312) 353 9685
Canova	Judy	Senior Scientist	SCDHEC-BLWM	2600 Bull St.	Columbia	SC	29201	(803) 896-4046
Capiro	Mirtha	Environmental Scientist	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 866-7567
Cerami	Jim		Chicago-Kent College of Law	565 West Adams St.	Chicago	IL	60661	(847) 508-0905
Chinn	Howard	Engineer	Illinois Attorney General's Office	188 W. Randolph St. 20th Floor	Chicago	IL	60601	(312) 814-5393
Claridge	Tom	Senior Project Engineer	Phepls Dodge Corporation	9780 East Sanchez Road	Safford	AZ	85546	(847) 397-7060
Clayton	Zachery	Project Manager	Environmental Design International, Inc	200 South Michigan Ave.	Chicago	IL	60604	(312) 356-5400 ext. 128

Last Name	First Name	Title	Company/ Affiliation	Address 1	City	State	Zip Code	Phone Number
Couch	Neil	Staff Professional	GeoSyntec Consultants	55 West Wacker Drive , Suite 1100	Chicago	IL	60601	(312) 658-0500
Davis	Suzanne	Hazardous Substances Engineer	CalEPA/DTSC	1001 I Street 12th Floor	Sacramento	CA	95814	(916) 327-4206
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Freed	Elisabeth	Environmental Protection Specialist	US EPA, HQ, Office of Site Remediation Enforcement	US EPA 1200 Pennsylvania Ave NW	Washington	DC	20460	(202) 564-5117
Feely	Patricia	Project Manager	Environmental Design International, Inc.	200 South Michigan Ave.	Chicago	IL	60302	(312) 356-5400
Gailey	Chad	Geologist	Black & Veatch	101 North Wacker Dr.	Chicago	IL	60606	(312) 683-7857
Gill	Micheal	ORD Superfund & Technology Liaison to Region 9	US EPA, Region 9	75 Hawthorne St.	San Francisco	CA	94105	(415) 972-3054
Griffin	Martin	Research Scientist	Wisconsin Department of Natural Resources Science Operations Ctr	2801 Progress Rd.	Madison	WI	53716- 3339	(608) 221-6370
Hansen	Michael	Principal Engineer	ARCADIS	6 Terry Drive Suite 300	Newtown	PA	19067	(267) 685-1800
Henry	Mark	Senior Environmental Engineer	Michigan Department of Environmental Quality	525 West Allegan	Lansing	MI	48933	(517) 335-3390
Jazdanian	Andy	Manager of New Business Development	TODA American Inc.	1920 North Thoreau Dr. Suite 110	Schaumburg	IL	60173	(847) 397-7060
Jolliet	Olivier	Associate Professor	University of Michigan	109 South Observatory	Ann Arbor	MI	48109	(734) 647-0394
Journey	Shane	Doctoral Student	University of Saskatchewan					
Karn	Barbara	Environmental Specialist	US EPA, ORD	1200 Pennsylvania Ave. N.W. 5205P	Washington	DC	20460	(202) 343-9704
Khodadoust	Amid							



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Leonova	Larisa	Chemist/ QA Coordinator	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 353-5838
Levin	Ida	QA Team Leader	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-6254
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Li	Xiaoqin		Lehigh University	13 East. Packer Ave.	Bethlehem	PA	18015	(610) 758-4519
Logan	Mary	RPM	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-4699
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Mayka	James	Chief, Innovative Systems & Technology Branch	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60604	(312) 353-9229
Mazur	Barbara	Ecologist	US EPA, Region 5 Office of Science Ecosystems & Communities	77 West Jackson Blvd.	Chicago	IL	60604	(312) 886-1491
McGovern	Greg	Project Manager	Earth Tech, Inc.	10 S. Riverside Plaza Suite 1900	Chicago	IL	60606	(312) 777-5432
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Last Name	First Name	Title	Company/ Affiliation	Address 1	City	State	Zip Code	Phone Number
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Ostrodka	Steve	Chief, Field Servies Station	US EPA, Region 5	77 West Jackson Blvd.	Chicago	IL	60514	(312) 886-3011
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