QEEN Workshop

Quantifying Exposure to Engineered Nanomaterials from Manufactured Products

Addressing Environmental, Health, and Safety Implications

Sponsored by the

Consumer Product Safety Commission (CPSC)

in collaboration with the

National Nanotechnology Initiative (NNI)

July 7-8, 2015
Rosslyn, VA, USA

Workshop Agenda

Quantifying Exposure to Engineered Nanomaterials from Manufactured Products

Addressing Environmental, Health, and Safety Implications

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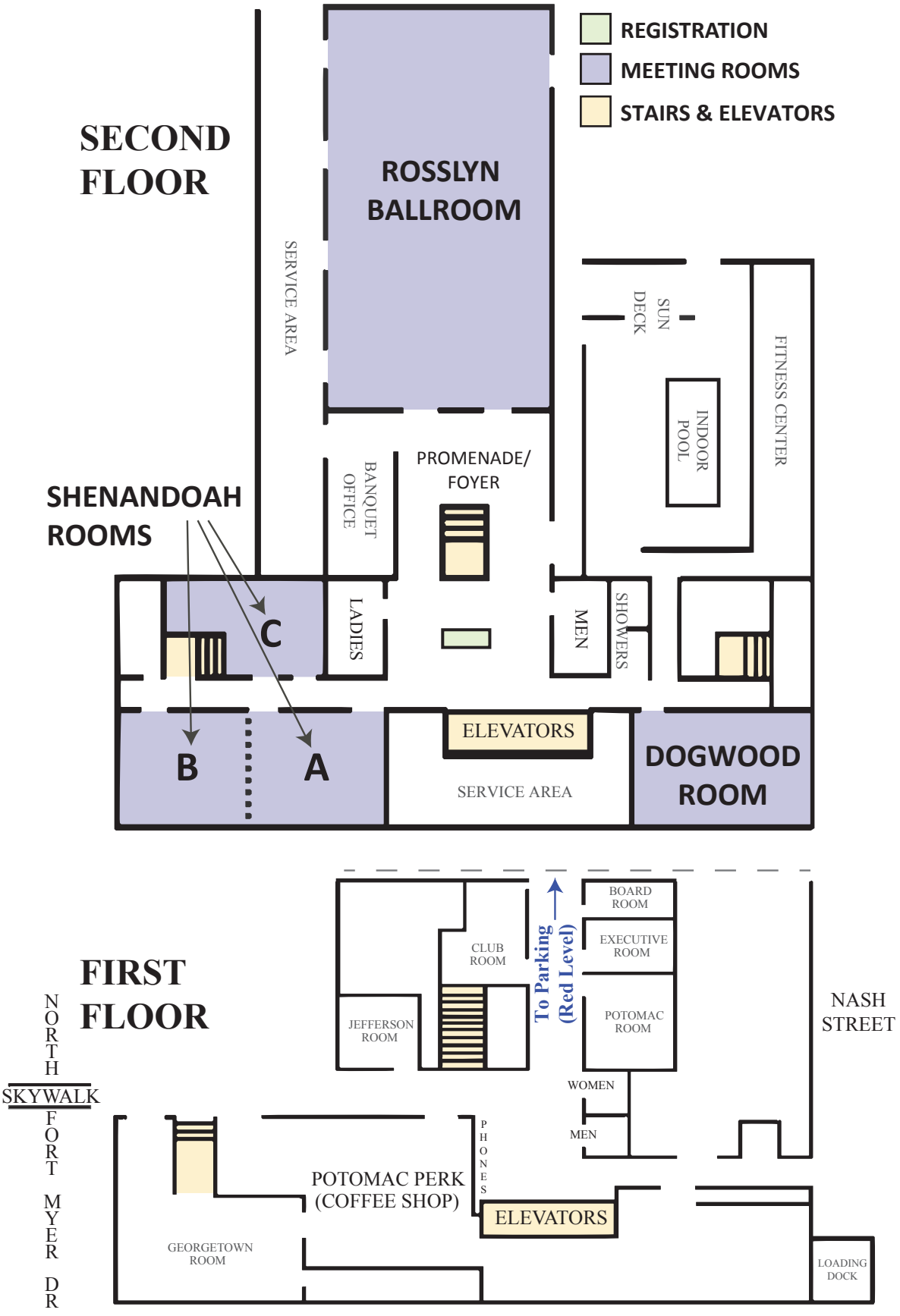

Quantifying Exposure to Engineered Nanomaterials from Manufactured Products

Addressing Environmental, Health, and Safety Implications

Agenda

July 7th — **Day One Plenary: Quantifying Exposure Across the Life Cycle**

Time		Session	Speaker		Location
8:00		*Registration*			2nd Floor Foyer
Morning Plenary Moderator: Treye Thomas (CPSC)					Rosslyn Ballroom
8:30-9:00	101 💻	**Welcoming Remarks**	**Treye Thomas**, *Leader, Chemical Hazards Program (CPSC)*; **Lloyd Whitman**, *Assistant Director, Nanotechnology (OSTP)*; **George Borlase**, *Assistant Executive Director, Hazard Identification and Reduction (CPSC)*		
9:00-9:45	102 💻	**Introduction:** The application of exposure science to the consumer product life cycle	***Paul Westerhoff*** *Arizona State University*	Pg. 6	
9:45-10:30	103 💻	**Occupational Exposure:** Review of the state of the science	***Chuck Geraci*** *NIOSH*	Pg. 6	
10:30-10:40		*Morning Break*			2nd Floor Foyer
10:40-11:25	104 💻	**Consumer Exposure:** Health risk driven exposure assessment for consumers during the life cycle of nanomaterial-containing products	***Jim Zhang*** *Duke University*	Pg. 7	Rosslyn Ballroom
11:25-12:10	105 💻	**Ecological Exposure:** Review of the state of the science	***Bernd Nowack*** *Empa*	Pg. 8	
12:10-13:30		*Lunch on your own*			
13:30-15:35		**Concurrent Sessions**	**Session Co-Chairs**		**Room**
	106A	**Worker Exposure Studies**	Kevin L. Dunn (NIOSH) and Bruce Lippy (CPWR)	Pg. 9	Dogwood
	106B	**Consumer Exposure Studies I:** General Products	Marina Vance (Vtech) and Keana Scott (NIST)	Pg. 9	Shenandoah A
	106C	**Consumer Exposure Studies II:** Food, Food-Contact, and Personal Care Products	Tim Duncan (FDA) and Margaret Kraeling (FDA)	Pg. 9	Shenandoah B
	106D	**Ecological and General Population Exposure Studies**	Elijah Petersen (NIST) and Jeff Steevens (USACE)	Pg. 9	Shenandoah C
	106E 📻	**Roundtable—Exposure Science in the 21st Century:** How its principles can transform safe and sustainable innovation and development of nanomaterial products *Moderator: Treye Thomas (CPSC)*		*See page 3 for session speakers*	Rosslyn Ballroom
15:35-15:45		*Afternoon Break*			2nd Floor Foyer
Afternoon Plenary Moderator: Janet Carter (OSHA)					Rosslyn Ballroom
15:45-17:15	107 💻	**Concurrent Sessions Roundtable**	Comparison of exposure assessment in different receptor populations		
17:15-17:30	107.5 💻	**U.S.-EU Collaboration on Exposure:** The *Exposure Through Product Life* CoR	***Martie van Tongeren*** *Institute of Occupational Medicine* & ***Rick Canady*** *NeutralScience L3C*	*Pg. 10*	
17:30-19:00	108	**Evening Poster Session** Featuring the *QEEN New Investigator Award* Poster Competition		*See page 5 for poster titles*	

💻 Indicates presentation will be webcast at http://www.tvworldwide.com/events/nnco/150707/

📻 Indicates recorded but no live webcast.

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July 8th — **Day Two Plenaries: Quantifying Exposure in Various Media and Pathways**

Time		Session	Speaker		Location
8:00		*Registration*			2nd Floor Foyer
Morning Plenary Moderator: Debbie Kaiser (NIST)					Rosslyn Ballroom
8:30-9:15	201 💻	**Introduction:** Measuring and modeling exposures to nanomaterials in complex systems	***Greg Lowry*** *Carnegie Mellon University*	Pg. 11	
9:15-10:00	202 💻	**Airborne Exposure:** Linking life cycle specific exposures to biological impact of nanomaterials	***Phil Demokritou*** *Harvard School of Public Health*	Pg. 11	
10:00-10:45	203 💻	**Waterborne Exposure:** Environmental multimedia distribution of nanomaterials	***Yoram Cohen*** *UCLA CEIN*	Pg. 12	
10:45-11:00		*Morning Break*			2nd Floor Foyer
11:00-11:45	204 💻	**Exposure in Biological Systems:** Review of the state of the science	***Christie Sayes*** *Baylor University*	Pg. 12	Rosslyn Ballroom
11:45-13:00		*Lunch on your own*			
13:00-15:05	**Concurrent Sessions**		**Session Co-Chairs**		**Room**
	205A	**Exposure Studies in Gaseous Media**	Vince Castranova (WVU) and Gedi Mainelis (Rutgers)	Pg. 12	Shenandoah C
	205B	**Exposure Studies in Aqueous Media**	Jeff Steevens (USACE) and Richard Zepp (EPA)	Pg. 1313	Shenandoah A
	205C	**Exposure Studies in Biological/Tissue/Serum**	Elijah Petersen (NIST) and Will Boyes (EPA)	Pg. 13	Shenandoah B
	205D	**Epidemiology: The Exposure-Health Interface**	Mary Schubauer-Berigan (NIOSH) and Sara Brenner (CNSE)	Pg. 13	Dogwood
	205E 💻	**New Investigator Interviews: What excites you about exposure science?** Featuring the *QEEN New Investigator Award* winner *Moderator: Chuck Geraci (NIOSH)*			Rosslyn Ballroom
15:05-15:15		*Afternoon Break*			2nd Floor Foyer
Afternoon Plenary Moderator: Cathy Fehrenbacher (EPA)					Rosslyn Ballroom
15:15-16:45	206 💻	**Concurrent Sessions Roundtable**	Comparison of exposure assessment in various media and bridging exposure science with toxicology		
16:45-17:30	207 💻	**Concluding Remarks**	**Treye Thomas** (CPSC)		

See page 4 for session speakers

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Quantifying Exposure to Engineered Nanomaterials from Manufactured Products

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July 7th — **Day One Concurrent Sessions: Receptor Populations**

Time	Room	106A: Worker Exposure Studies Pg. 14 — Dogwood	106B: Consumer Exposure Studies I: General Products Pg 16 — Shenandoah A	106C: Consumer Exposure Studies II: Food, Food-Contact, and Personal Care Products Pg 18 — Shenandoah B	106D: Ecological and General Population Exposure Studies Pg.20 — Shenandoah C	106E: Roundtable—Exposure Science in the 21st Century — Rosslyn Ballroom
13:30	**Co-chairs**	**Kevin L. Dunn (NIOSH) & Bruce Lippy (CPWR)**	**Marina Vance (Vtech) & Keana Scott (NIST)**	**Tim Duncan (FDA) & Margaret Kraeling (FDA)**	**Elijah Petersen (NIST) & Jeff Steevens (USACE)**	**13:30-14:25** Roundtable with Paul Lioy (Rutgers) Chuck Geraci (NIOSH) Greg Lowry (CMU) and Tina Bahadori (EPA)
13:35-13:55	**Speaker 1**	Stephan Froggett (Froggett & Associates LLC)	Jo Anne Shatkin (Vireo Advisors)	Jay Ansell (Personal Care Products Council)	Paul Westerhoff (Arizona State University)	
13:55-14:15	**Speaker 2**	Dhimiter Bello (UMass Lowell)	Gediminas Mainelis (Rutgers University)	Stephen Ebbs (Southern Illinois University)	Brian Mader (3M)	
14:15-14:35	**Speaker 3**	Matthew Dahm (USPHS/NIOSH)	Marina Vance (Virginia Tech)	Roland Franz (Fraunhofer Institute for Process Engineering & Packaging)	Karen Murphy (NIST)	*Break*
14:35-14:55	**Speaker 4**	Gary Casuccio (RJ Lee Group)	Keana Scott and Li-Piin Sung (NIST)	Linda Katz (FDA)	Jason White (Connecticut Agricultural Experiment Station)	**14:40-15:35** Town Hall
14:55-15:05	*Break*					
15:05-15:35	**Panels**	**Speaker Panel**	**Speaker Panel**	**Speaker Panel**	**Speaker Panel**	
15:35-15:45	*Break*					
15:45-17:15	**Concurrent Sessions Roundtable**	**Comparison of exposure assessment in different receptor populations** (Rosslyn Ballroom)				

Quantifying Exposure to Engineered Nanomaterials from Manufactured Products

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July 8th Day Two Concurrent Sessions: Media and Pathways

Time	Room	205A: Exposure Studies in Gaseous Media Pg. 23 Shenandoah C	205B: Exposure Studies in Aqueous Media Pg. 25 Shenandoah A	205C: Exposure Studies in Biological/Tissue/Serum Pg. 27 Shenandoah B	205D: Epidemiology: The Exposure-Health Interface Pg 29 Dogwood	205E: New Investigator Interviews Rosslyn Ballroom
13:00	**Co-Chairs**	**Vince Castranova (WVU) & Gedi Mainelis (Rutgers)**	**Jeff Steevens (USACE) & Richard Zepp (EPA)**	**Elijah Petersen (NIST) & Will Boyes (EPA)**	**Mary Schubauer-Berigan (NIOSH) & Sara Brenner (CNSE)**	**13:05-14:00** Students and Postdoctoral Associates and *QEEN New Investigator Award* Winner by Chuck Geraci
13:05-13:25	**Speaker 1**	Jonathan Thornburg (RTI International)	Chris Knightes (EPA)	Kim Rogers (EPA)	Mary Schubauer-Berigan (NIOSH)	
13:25-13:45	**Speaker 2**	Phil Demokritou (Harvard School of Public Health)	Steve Diamond (NanoSafe)	Monique Johnson (NIST)	Sara Brenner (SUNY Albany)	
13:45-14:05	**Speaker 3**	Phoebe Stapleton (WVU School of Medicine)	Greg Noonan (FDA)	Katherine Tyner (FDA)	Adam Friedman (Einstein College of Medicine)	*Break*
14:05-14:25	**Speaker 4**	Vincent Castranova (WVU School of Pharmacy)	Howard Fairbrother (Johns Hopkins University)	Robert Mercer (NIOSH)	**Speaker Panel**	**14:10-15:10** Students and Postdoctoral Associates
14:25-14:35	*Break*					
14:35-15:05	**Panels**	**Speaker Panel**	**Speaker Panel**	**Speaker Panel**		
15:05-15:15	*Break*					
15:15-16:45	**Concurrent Sessions Roundtable**	**Comparison of exposure assessment in various media: Bridging exposure science with toxicology** (Rosslyn Ballroom)				

July 7th **Posters** **Rosslyn Ballroom**

Poster	Title	Authors	Pg #	*
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108.02	SERENADE An 8 year French funding safe(r) by design project. Introducing consumer exposure case studies	J.Rose, J-Y Bottero, A. Masion, S. Pekar-Bonifay, and C. de Garidel-Thoron	32	
108.03	Quantifying toxicity levels of engineered colloidal silica nanoparticles used in semiconductor manufacturing	K. Kosaraju, M. Tarannum, S. Crawford, and S. Aravamudhan	33	*
108.04	A nano-architectured electrode for a high-performance supercapacitor	Y. Liu, A. Aboagye, L. Zhang, and J. Wei	33	*
108.05	Quantifying silver nanoparticle release from commercially available consumer products	A. Mackevica, M. Olsson, and S. Foss Hansen	34	*
108.06	Testing strategy to measure exposure throughout the life cycle	A. Masion, M. van Tongeren, and J. Rose	34	
108.07	Release of copper nanoparticles from pressure-treated lumber through simulated dermal contact	W. Platten, N. Sylvest, C. Warren, M. Arambewela, S. Harmon, K. Bradham, K. Rogers, T. Thomas, and T. Luxton	35	
108.08	Development of a sensitive assay to detect and characterize the effects of nanomaterials on aquatic ecosystems using an *ex vivo* preparation of crustacean olfactory receptor neurons	J. Plotkin and C. Kepley	35	*
108.09	Release of silver nanoparticles from nano-enabled water treatment membranes across the product's life cycle	J. Rice, A Barber, T Zaikova, J Hutchinson, and M Wiesner	36	*
108.10	Physical-chemical state and mechanisms of nanomaterial release from products during their life cycle: Self-cleaning cement and acrylic wood coating case studies	L. Scifo, N. Bossa, A. Avellan, P. Chaurand, D. Borschneck, C. Levard, O. Aguerre-Chariol, J. Vicente, C. Geantet, M. Auffan, D. Borschneck, J. Labille, J-Y Bottero, and J. Rose	36	
108.11	Toxicological comparison of *in vitro* exposure techniques of commercial nano products to lung cells	L. Secondo and N. Lewinski	37	*
108.12	Nano-waste: environmental health and safety implications during thermal degradation/incineration of nano-enabled products at their end-of-life	D. Singh, G. Sotiriou, F. Zhang, W. Wohlleben, and P. Demokritou	38	*
108.13	Risk evaluation of silver nanoparticle exposure from antibacterial spray containing silver nanoparticles	E. Kim, J-H Lee, J-K Kim, G-H Lee, K. Ahn, J-D Park, and I-J Yu	39	
108.14	A case study on risk evaluation of printed electronics using nanosilver ink	E. Kim, J-H Lee, J-K Kim, G-H Lee, K. Ahn, J-D Park, and I-J Yu	39	
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108.18	Nanotechnology for sensors and sensors for nanotechnology: improving and protecting health, safety, and the environment — Nanotechnology Signature Initiative	S. Lehrman	41	
108.19	Revisiting the safety of food-grade nanomaterials: Towards more realistic and relevant studies	I. Sohal, D. Nida, K. Racicot, K. O'Fallon, A. Pal, R. Nagarajan, L. Samuelson, and D. Bello	42	

* Travel Award Recipient and QEEN New Investigator Award Competition entries

Abstracts and Descriptions

Plenary Abstracts and Concurrent Session Descriptions

Tuesday

102 The application of exposure science to the life cycle

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Research tools and data related to assessing nanomaterial toxicity (hazard) has advanced more rapidly than in the field of exposure assessment of nanomaterials. This presentation addresses four central questions, each providing the opportunity to show the state of science, who is collecting what types of data and by using which methods, and where are gaps that the exposure community should address to assure safe development of nanotechnology. First, a state of the science related to nanomaterial exposure compares publication trends, definitions and dosimetry approaches for nanomaterials. The second portion of the presentation addresses what data and methods are available for releases of nanomaterials from products across the life cycle from the point of synthesis through workplace exposures, consumer product usages and end of life. After a discussion on nanomaterial usage by different sectors, detailed examples of taking a life cycle view is given for NMs used in industrial processing, dispersed in foods/gels/creams, embedded in polymers, or attached to flexible surfaces (e.g., textiles). These discussions highlight what we know, and don't know, about factors affecting NM release and transformation and how they interact with humans and then environment. Some attention is given to the beneficial aspects of nanomaterials, and that NMs may reduce exposure to more toxic organic chemicals potentially being replaced in some products. A brief overview of concepts and advances in NM exposure modeling concludes this section. The third portion of the presentation introduces the existing tools and emerging challenges around techniques to detect, extract and quantify NMs in complex matrices (products, tissues, and biological fluids). The availability of the analytical techniques and potential strategy to included a tiered sampling approach is described, but hinges upon acceptable detection limits. Challenges are identified to detect engineered NMs amidst many times higher number concentrations of natural and/or incidental NMs. The presentation concludes by summarizing what the existing exposure science is telling us in where data gaps and research needs exist. A major conclusion is that nano-specific human exposure models and scenarios have been developed and validated, and whereas we have reams of in vitro toxicity data we lack data on NM bio-distribution, bio-availabity and bio-accumulation in humans exposed to NMs via different routes.

103 Occupational Exposure: Current state, challenges, and future research

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The introduction of engineered nanomaterials into commercial material applications continues at a rapid pace, despite the overall evolution of the technology now having moved from the initial excitement stage to that of a pace driven by more realistic market forces. High-volume manufacture and formulation of 'first-generation' nanomaterials, such as nanoscale Titania and Ceria, continues globally. Refinement and improvement of manufacturing processes for more sophisticated and promise-filled nanomaterials, such as carbon nanotubes and graphene, are being reported almost daily. All of these indicators point to increasing volumes of engineered nanomaterils being manufactured and an even greater number of product applications for these materials. One of the natural outcomes of this continued rise in volumes and product applications is concern for human and environmental safety. Whether in a research laboratory, a manufacturing facility, as part of a

commercial task, or in the reuse or recycle of these materials, there are workers involved. At nearly every step along the life cycle of an engineered nanomaterial and the products that contain them, there is potential for workers to be exposed. Evaluating worker exposure is critical to ensuring responsible development of the technology because workers represent the first opportunity for human exposure to any new technology or the materials it produces. In many cases the materials may not be completely characterized and their potential hazards not fully understood. In many ways, creating an effective worker health and safety program for a new technology or material is the first step in building a legacy of success for responsible development, sustainability, and stewardship.

In order to begin evaluating the potential risk for any occupational setting involving engineered nanomaterials it is extremely important to develop effective exposure assessment science that focuses on properties and behaviors that are characteristic, if not unique to this class of materials. Such an approach links toxicology, risk assessment, and epidemiology to create a complete picture of the potential risks and impacts. Hazard information from toxicology studied is being generated a rapid pace for many nanomaterials. The rise of hazard data and efforts to derive Occupational Exposure Limits has accelerated efforts to evaluate occupational exposures. Despite the progress in recent years with measurement techniques for nanomaterials, there still remains a lot of uncertainty as to the appropriate exposure metric to use. This uncertainty is compounded by the growing number of dose metrics being proposed for toxicology evaluations, especially for inhalation studies; a primary expouse pathway in the workplace. A basic strategy that uses multiple sampling, analytical, and instrumental approaches will be discussed.

A number of workplace exposure assessment strategies have been proposed by several groups around the globe. Employing a multi-metric and tiered or phased approach has become one of the more effective approaches. A basic challenge continues to be the nature of the material being measured in the workplace as compared to the seemingly same material evaluated in toxicology studies. Efforts are underway in several research institutes to close the gap between nanomaterials encountered in the workplace or the environment and those that are evaluated in their pure (pristine) state. These efforts are aimed at making the toxicology evaluations more representative of what is encountered in an actual exposure scenario. This area of research will improve workplace exposure science by linking the efforts of toxicology, exposure measurement, and epidemiology based health outcome studies. By creating a dialogue and feedback process from exposure measurements to toxicology studies, dose metrics and test materials will become more representative and risk characterizations more realistic. Combining health outcome studies into the overall strategy incorporates the use or biological indicators, such as biomarkers, for an even more complete picture of the actual exposure experience.

Finally, the potential release of engineered nanomaterials from intermediate or finished products has become a growing concern. Research is underway by several groups to evaluate the impact this additional element in evaluating the overall potential for exposure to engineered nanomaterials along their complete life cycle. While the biological significance of the presence of these material in any sort of release in not known, a prudent approach is to characterize the potential for release and explore methods to minimize or control releases.

104 Health risk driven exposure assessment for consumers during the life cycle of nanomaterial-containing products

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Engineered nanomaterials (ENMs) have been increasingly used in numerous consumer products with a goal to enhance the usability or effectiveness of the products. The addition of ENMs into a consumer product may affect consumers' exposure to ENMs and associated chemicals along the life cycle of the consumer product. The objective of this presentation is to provide a review of major factors that affect consumers' exposure based on a comprehensive risk assessment framework that is used in a US-UK consortium, namely the 'Risk Assessment for Manufactured Nanoparticles Used in Consumer Products (the RAMNUC Project)'. Based on the over-arching hypothesis that ENMs at the point of exposure for both humans and aquatic animals may substantially differ in both

physicochemical and toxicological properties from the ENMs originally added into the consumer product, the RAMNUC project characterizes physiochemical and toxicological properties of ENMs and associated chemicals to which consumers can be actually exposed. With a focus on the inhalation exposure pathway, the presentation will report findings of the RAMNUC project on selected consumer spray products that incorporate nano zinc oxide and nano silver as well as a diesel fuel additive containing cerium dioxide nanoparticles. A unique feature of the RAMNUC approach is that data generated from laboratory-based experiments are integrated into mechanism-based computational modules of source-to-exposure-to-dose-to-effects modeling systems, allowing for rational extrapolation and generalization in ENM exposure and risk assessment.

105 Ecological Exposure: Review of the state of the science

Bernd Nowack
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The current and future widespread usage of engineered nanomaterials (ENM) in industrial applications and consumer products will inevitably cause emissions of ENM to the environment and result in an increase of environmental exposure. As a starting point for an environmental exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where the environment may face exposure to ENM. By tracking the life cycle of products, it is possible to explore whether and in which situations a release of ENM from applications may occur. This presentation shows that using material flow and environmental fate modeling as basis, we can quantitatively identify the determining steps in the life cycle of nano-products that result in release to the environment. Within the environmental exposure assessment, two very critical points with limited data are the knowledge about production amounts of ENM and the distribution of the ENM to different product categories. Also the release of ENM from actual products has been studied only to a limited extent. Such studies not only need to quantify the amount released, but also characterize the released materials. Only a certain fraction of the released materials are actually in the original form and also in the nano-sized range (depending on the starting materials). The results from material-flow models incorporating knowledge on production, use and release, can be used to get first information on environmental concentrations using simple box models. The modeled flows can also be used as input for mechanistic environmental fate models that can provide more accurate descriptions of environmental concentrations. Finally is it shown how exposure modeling can be linked to modeling of the environmental effects of ENM to derive first environmental risk assessments for ENM.

106A Worker Exposure Studies

Dogwood Pg. 14

Co-Chairs: Kevin Dunn[1] and Bruce Lippy[2]

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[2] *CPWR — The Center for Construction Research and Training, 8484 Georgia Avenue, Suite 1000, Silver Spring, MD 20910,* blippy@cpwr.com

This session will address the relatively limited literature on worker exposures by beginning with a broad overview of 54 studies on release of nanomaterials from solid nanocomposites along the life cycle from drilling and sanding to eventual shredding, incineration and composting. The next presentation will explore in greater detail the techniques for measuring releases from nanocomposites. Recent NIOSH findings on worker exposures to carbon nanotubes and nanofibers will then be presented followed by a review of an innovative thermophoretic personal sampler for collecting airborne nanoparticles on a grid for direct analysis by transmission electron microscopy.

106B Consumer Exposure Studies I: General Products

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Co-Chairs: Marina Vance[1] and Keana Scott[2]

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In this session, we will discuss several recent studies on the release of nanomaterials from consumer products, focusing on the methods and techniques used, the challenges associated with different types of nanomaterials and matrices, and how these efforts may help facilitate evaluation and adoption of new nanomaterials into existing as well as novel products.

106C Consumer Exposure Studies II: Food, Food Contact and Personal Care Products

Shenandoah B Pg. 18

Co-Chairs: Timothy Duncan[1] and Margaret Kraeling[2]

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[2] *US Food and Drug Administration, CFSAN/OARSA/DT/DRTIB (HFS-025), 8301 Muirkirk Road, Laurel, MD 20708,* margaret.kraeling@fda.hhs.gov

Selected topics in this session include potential exposure to nanocomposite food packaging, engineered nanomaterials used in consumer food and/or agricultural products (e.g., fresh produce), sunscreens, and cosmetics. Speakers will report on their efforts to investigate the potential routes of exposure (ingestion, skin absorption, etc.), to measure the quantity and morphology of ingested/absorbed particles, to develop methods to ensure relevant exposure data can be obtained, and to formulate and test predictive exposure models.

106D Ecological and General Population Exposure Studies

Shenandoah C Pg. 20

Co-Chairs: Elijah Petersen[1] and Jeff Steevens[2]

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[2] *US Army Engineer Research and Development Center Environmental, Laboratory ATTN CEERD-EZ-S, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199,* jeffery.a.steevens@usace.army.mil

This session focuses on the emerging methods that address the challenges with characterizing exposure in the complex natural and built environment. These challenges include a wide range of matrices that have the potential to transform nanoparticles released into the environment and complicate an accurate characterization of relevant properties. Presentations will emphasize how these methods can be used to overcome these challenges to accurately assess availability and exposure.

107.5 U.S.-EU Collaboration on Exposure: The *Exposure through Product Life* Community of Research

Martie van Tongeren[1]* and Rick Canady[2]

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[2] *NeutralScience L3C, Washington, DC*

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Exposure assessment is critical part of health and environmental risk assessment, without which it is difficult if not impossible to study the determinants of risk as well as controlling and managing these risks. It is wide recognized that exposure assessment in the field of nanotechnology is extremely complicated, specifically when carried out in complex exposure scenarios. Hence, it is essential that resources are allocated to develop/adapt tools and methodologies that can be applied in a cost effective way, without non-essential duplication of effort. Considering that resources are limited, collaboration and coordination between scientists is essential.

Within the EU the number of nanosafety projects that focus or include exposure assessment elements have grown considerably over the years. A number of projects have been funded that focus predominantly on exposure assessment (e.g. NANODEVICE, NANEX, NANOINDEX, and most recently NANOFASE). Within the European NANOSAFETY CLUSTER, Working Group 3 focuses on exposure assessment and aims to promote improvement and harmonization of methods through sharing of project methods, techniques/results/data and coordinate relevant cross-project activities.

The NANORELEASE project is an example of a cross-continental collaboration that aimed to foster the safe development of nanomaterials by supporting development of methods to understand the release of nanomaterials used in products. The project focussed on two areas (food and plastics) and received funding form over 10 sources, with participating from dozens of countries. Examining lessons learned from this project is useful in setting up similar transnational consortia.

The EU-US Community of Research (CoR) working groups were set up several years ago to promote and facilitate and coordinate collaboration between EU and North American researchers in the field of nanotechnology environment, health and safety. One of these CoRs focussed on the area of exposure assessment. The group has met during various workshops over the last 3 to 4 years, but so far it didn't manage to develop a coherent programme of work. The challenge of the Exposure CoR is to build upon the success of NANORELEASE and maintain existing links and develop further collaborations. The CoR is seeking to establish a core group of 4-8 people coving the various exposure disciplines and develop a more active workplan in areas such as methods and tools, database and data sharing. We will work closely with other CoRs (eg data base, modelling, risk assessment, etc). Providing incentives is important to encourage participation in the CoRs and we will seek to identify opportunities for join funding, papers and workshops/conferences. The QEEN workshop clearly provides an excellent opportunity to establish the foundations of the Exposure CoR.

Plenary Abstracts and Concurrent Session Descriptions

Wednesday

201 Measuring and modeling exposures to nanomaterials in complex systems

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Exposure assessment for engineered nanomaterials used in consumer products is an essential part of assessing their risks to consumers and to the environment. Accurate exposure assessment is confounded by the enormous variation and complexity of nanomaterials, product matrices and uses, system conditions, and estimates of sources and exposure pathways. Despite this complexity, there are fundamental processes that most affect releases and fate process that can be incorporated into fate and exposure modeling. These processes are identified using a systematic integrated experimental approach in well-controlled systems, systems with managed complexity and "real" systems to confirm that the identified processes indeed control the behavior of the nanomaterials in a real environment. Central to this integrated experimental approach is development of characterization tools, the use of a centralized large scale "real" test facility, and the early development of models can be used to integrate and focus research efforts towards a common goal of developing and refining accurate exposure models and measurement methods. I will present the refinement of this approach using lessons learned from ten years of environmental exposure assessment for nanomaterials, and relate how these can inform efforts for assessing exposures to nanomaterials in consumer products. The primary focus will be on the experimental approaches, transformations of nanomaterials, and how these transformations affect characterization methods needed to accurately assess nanomaterial exposures. Critical gaps in knowledge that hinder these assessments are laid out as well as a plan to address those gaps.

202 Linking life cycle specific exposures to biological impact of nanomaterials

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Incorporation of Engineered nanomaterials (ENMs) in Nano-enabled products (NEPs) is growing exponentially. Such increased consumer use and disposal of NEPs at their end of life has led to inevitable environmental and human exposures raising concerns for potential Environmental, health and safety (EHS) implications associated with ENMs released across the life cycle of NEPs. However, current nano-risk assessment paradigm focuses primarily on the properties of pristine ENMs used in the synthesis of NEPs rather than the actual properties of the particulate matter released across the NEP life cycle (called LCPM). Indeed, the potential for exposure from such life cycle particulate matter (LCPM) may exceed that of pristine ENMs at occupational level. Evidence continues to grow indicating that the physico-chemical properties and toxicological profiles of LCPM may also differ greatly from those of pristine ENMs. This life cycle specific exposure data gap constitutes a major roadblock for risk assessors and regulators and prohibits the sustainable development of nanotechnology industry. There is an urgent need to understand life cycle specific release/exposure scenarios for families of NEPs and assess potential EHS implications. More importantly, there is a need to develop new standardized methodologies and tools across the exposure-toxicological characterization-disease continuum of NEPs for risk assessment.

This presentation will focus on the interface of exposure science and nanotoxicology and discuss the state of science, knowledge gaps and critical issues and challenges for nanosafety research. An overview of recently developed tools and integrated methodologies that can be used to link "real world" exposures across life cycle of NEPs to toxicology and disease will be presented. An overview of the state of science in terms of development of exposure

systems and methods to assess nanoparticle release across life cycle of NEPs and their link to biological impact will also be presented. Examples of exposures at consumer level and at the end of life of commercially available NEPs along with the implementation of life cycle specific risk assessment approaches will be presented. *In toto*, revisiting the current risk assessment paradigm and developing all necessary tools and approaches to enable comprehensive risk assessment to include life cycle specific risks from NEPs is of paramount importance for the nanosafety field

203 Environmental multimedia distribution of nanomaterials

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Assessment of the potential environmental impact of engineered nanomaterials (ENMs) requires information regarding their concentrations in the various environmental media (e.g., water, sediment, air, soil, vegetation, biota). ENMs will disperse in the aquatic and atmospheric media, infiltrate the soil subsurface, and move across environmental phase boundaries due to intermedia transport processes. Given the large existing and rapidly growing number of different engineered nanomaterials (ENMs), practical approaches are needed (via both monitoring and modeling) to support the critical need of environmental impact assessment (EIA) of ENMs. Such approaches which should consider the behavior of ENMS in the multimedia environment will be reviewed in the present presentation. In particular, the state-of-the-art in modeling fate and transport of ENMs in aquatic media and multimedia distribution of ENMs will be discussed. Various approaches that have been advanced over the last several years for estimating potential environmental releases of ENMs and associated exposure concentrations will be reviewed including experimental laboratory and mesocosm fate and transport studies, environmental monitoring, and transport models developed at different scales. In addition, the merits of integrating methods of estimating the release of ENMs with exposure analysis and toxicity information will be discussed in relation to EIA for ENMs.

204 Exposure in biological systems: Review of the state of the science

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Exposure to nanomaterials and nanomaterial-enabled products is possible across the entire product life cycle. From research & development in workplace facilities to consumer use in homes to disposal processes at end-of-life, biological intake has been shown though inhalation, ingestion, and dermal exposures. This talk offers a review of the science in the areas related to human exposure, nanomaterial characterization, health effects, and exposure levels. Contaminant containment, hazard or health banding, and categorization frameworks can aid in mitigating exposures; but, measuring the exposure to biological systems is still an understudied area within the field of nano-EHS. Nanomaterial monitoring is often classified in one of three endpoints: personal, area, or biological. The most informative material monitoring is performed when both observing the physicochemical properties and measuring the quality/quantity of engineered materials occurs over a period of time. Biological monitoring measures contaminants, metabolites, or enzymes in individual's blood, urine, or exhaled breath. Together with personal and area monitoring, biological monitoring can result in quantifying exposure to engineered nanomaterials. Ultimately, the nano-EHS community should develop a graded approach to measurement which can include (1) screening areas and processes, (2) collecting samples at source and personal space, and (3) analyzing biological fluids for changes in biomarker levels in acute and chronic phenotypical responses. Some of these responses include inflammation, sensitization/irritation, and lung/cardiovascular/liver damage. It makes sense to control exposure to those nanomaterials for which preliminary hazard data has already shown unwanted health effects or for those nanomaterials where the hazards are unknown. When it comes to human exposure, measuring markers in biological systems is a useful tool in moving exposure science, toxicology, and nanotechnology forward.

205A Exposure Studies in Gaseous Media

Shenandoah C Pg. 23

Co-Chairs: Vincent Castranova[1] and Gedi Mainelis[2]

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The goals of this session are to characterize airborne levels, size distribution and composition of nanoparticles generated during production and use of nanomaterials. The adverse biological responses to exposure to these nanoparticles will be evaluated and time course and dose-response described.

205B Exposure Studies in Aqueous Media

Shenandoah A Pg. 25

Co-Chairs: Jeff Steevens[1] and Richard Zepp[2]

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Aqueous systems are an important phase in the release and exposure to nanoparticles. This session includes four presentations across the continuum of release from nanomaterial containing products in aqueous media, predicting fate and transport in the aquatic systems, and characterizing aqueous exposure. New approaches and techniques will be discussed that advance exposure science in this universal medium.

205C Exposure Studies in Biological/Tissue/Serum

Shenandoah B Pg. 27

Co-Chairs: Will Boyes[1] and Elijah Petersen[2]

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This session focuses on the emerging methods that address the challenges with characterizing exposure in organism tissues and biological media such as serum. These complex matrices can complicate engineered nanomaterial quantification. Presentations will highlight methods for quantifying engineered nanomaterials and nanomaterial transformations in these matrices.

205D Epidemiology: The Exposure-Health Interface

Dogwood Pg. 29

Co-Chairs: Mary Schubauer-Berigan[1] and Sara Brenner[2]

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This session will feature researchers conducting state-of-the-science studies of exposure and associated measures or indicators of possible early health effects among workers and others exposed to engineered nanomaterials. It is anticipated that this session will raise awareness among other disciplines of the importance of incorporating appropriate physical, chemical, and route-of-exposure metrics to studies of health effects in those exposed to engineered nanomaterials, and will identify research needed to correlate exposure data and health effects.

Concurrent Session Abstracts

Tuesday

106A Worker Exposure Studies

Dogwood

Co-Chairs: Kevin Dunn[1] and Bruce Lippy[2]

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This session will address the relatively limited literature on worker exposures by beginning with a broad overview of 54 studies on release of nanomaterials from solid nanocomposites along the life cycle from drilling and sanding to eventual shredding, incineration and composting. The next presentation will explore in greater detail the techniques for measuring releases from nanocomposites. Recent NIOSH findings on worker exposures to carbon nanotubes and nanofibers will then be presented followed by a review of an innovative thermophoretic personal sampler for collecting airborne nanoparticles on a grid for direct analysis by transmission electron microscopy.

106A.1 Development of a nanoparticle sampler for particle speciation using electron microscopy

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A portable thermophoretic nanoparticle sampler has been developed that deposits airborne ultra-fine particles directly onto an electron microscopy (EM) grid. The particles on the grid can be subsequently measured and speciated using EM techniques to provide an assessment of exposures. Particle collection efficiencies associated with the sampler were evaluated in laboratory experiments. These experiments, along with theory of thermophoretic velocity, were used to establish the collection efficiency of the sampler. The sampler has also been evaluated in field studies representative of real world conditions. Data are provided illustrating the potential of the sampler for use in exposure assessment. Comparisons to results obtained from scanning mobility particle sizer (SMPS) spectrometer are also provided.

106A.2 Carbon nanotube exposure assessment: An evaluation of workplace exposures in the U.S.

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Just as there has been much advancement in the field of toxicology over the past decade relative to potential health outcomes from carbon nanotube (CNT) exposures, similar strides are being made in the field of exposure assessment. Recent developments in sampling methodologies have led to more accurate estimates for worker exposure levels as compared to preliminary studies, which may have overestimated exposures. As part of an ongoing NIOSH exposure assessment and epidemiologic study, worker exposure to CNT has been examined by sampling 14 different worksites across the U.S. over a three year period. Personal breathing zone exposure levels were measured using a chemical specific marker for the mass concentration of elemental carbon (EC) at both the inhalable and respirable size fractions. Inhalable particles are generally less than about 100 micrometers (µm) in size and when these particles are breathed in, they can deposit in the nose, mouth, windpipe (trachea), and the upper portions of the lung. Respirable particles are less than about 4 µm in size and when they are breathed in, they can enter the deepest parts of the lung, the alveoli. The sampling methodologies are in accordance with the NIOSH Current Intelligence Bulletin on CNTs and carbon nanofibers which set a mass based Recommended Exposure Limit at 1 µg/m3 of EC at the respirable size fraction. Overall, personal workplace exposures at the respirable size fraction

to EC ranged from 0.02 – 2.94 µg/m3 with a geometric mean of 0.34 µg/m3 and an 8-hr TWA of 0.16 µg/m3. Inhalable personal breathing zone exposures ranged from 0.01 – 79.57 µg/m3 with a geometric mean of 1.21 µg/m3. Concurrent personal breathing zone samples were also collected and analyzed by electron microscopy using methods similar to the asbestos counting convention. These samples showed concentrations ranging from 0.0001 to 1.613 CNT or CNF-structures per cm3 with a GM of 0.008 and an 8-hr TWA concentration of 0.003. The most common CNT structure sizes were found to be larger agglomerates in the 2–5 µm range as well as agglomerates >5 µm. This study also focused on how exposure level and type change within the various industries in which CNTs are being applied (composites, electronics, production), between types of materials (multi-walled vs. single-walled), and under varying work conditions. The detailed information from these exposure assessment findings bring awareness to industries with higher exposure potentials and provide valuable data on job specific tasks where exposures are likely to occur.

106A.3 Do studies of release from manufactured nanocomposites inform potential for worker exposure?

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The addition of specific nanomaterials to conventional composites has been shown to enhance durability and strength, or to confer unique properties. Such nanocomposites have direct consumer and environmental benefits, but potential worker exposure during manufacture remains poorly understood. A review of the data from over fifty studies designed to specifically investigate release from manufactured nanocomposites yield little information in aggregate. Aside from the dearth of experimental studies, most analysis is further limited by the use of disparate methods and materials across these studies. Specifically, the methods used to induce release from nanocomposites in any setting have not been rigorously validated. Furthermore, the nanocomposites investigated in many of the studies are novel, lab-made materials with potentially no relevance to commercially viable nanocomposites. And finally, how the released debris correlate to real world conditions remains poorly understood.

What is known at this time is: (1) most solid nanocomposites will release particles of matrix alone, (2) a large subset of these will also release matrix particles with the added nanomaterial either partially or fully embedded; (3) release of the added nanomaterial, completely dissociated from the matrix is only infrequently observed; and (4) ionic forms of the nanomaterial are even more rarely detected. These data highlight that release from manufactured nanocomposites can take multiple forms. Importantly, as risk is considered to be a function of the inherent hazards of a substance and the actual potential for exposure, data on nanomaterial release dynamics and debris composition from commercially relevant nanocomposites are a valuable starting point for consideration in fate and transport modeling, workplace exposure assessment, and risk assessment frameworks for nanomaterials. Specifically, method validation and standardization, as well as understanding how laboratory release scenarios relate to real-world conditions would yield beneficial guidance, allowing for more consistent characterization of the release potential of nanomaterials and released debris composition.

106A.4 Exposures to nanoparticles and fibers during manufacturing, recycling, and post-processing of carbon nanotube-reinforced composites

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The presentation is based on a series of studies designed to investigate the feasibility of end-of-life recycling of CNT-reinforced nanocomposites and its impact on nanocomposite performance, worker exposures, and toxicity of real-world nanoparticle exposures during nanocomposite synthesis and recycling. A summary of exposures to airborne nanoparticles, carbon nanotubes (CNTs), and fibers generated during various tasks in the injection molding and recycling processes of polycarbonate (PC) and polypropylene (PP) composites reinforced with carbon nanotubes (CNT/PC and CNT/PP respectively) will be presented. Exposures during processing of neat PC and PP composites were evaluated for comparison purposes. Multiple metrics

were used to characterize exposures, including total number concentration and size distribution from 5.6 nm to 20 µm, nanoparticle and fiber morphology, respirable fiber classification and counting (long and short fibers), CNT quantitation, and integrated sampling for targeted chemical analysis. Similarly, nanocomposite performance was evaluated through serial measurements of structural chemical changes, rheological, thermal, and mechanical properties and crystalline behavior.

The presentation will summarize exposure data, explore the impact of recycling on exposures and performance, and discuss implications of these findings for exposure controls and quantitative exposure assessment to engineered nanoparticles in complex scenarios

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106B Consumer Exposure Studies I: General Products

Shenandoah A

Co-Chairs: Marina Vance[1] and Keana Scott[2]

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In this session, we will discuss several recent studies on the release of nanomaterials from consumer products, focusing on the methods and techniques used, the challenges associated with different types of nanomaterials and matrices, and how these efforts may help facilitate evaluation and adoption of new nanomaterials into existing as well as novel products.

106B.1 Potential inhalation exposures for nanoparticles due to the use of consumer products

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Presently, there are almost 2,000 nanotechnology-enabled consumer products on the market. Some of the product categories, such as sprays, cosmetic powders and clothing, have potential to release high concentrations of nanoparticles during their application, which could result in user exposures and possible health effects. However, the information on such exposures is limited.

In this study, concentration, size distribution, shape and agglomeration state of particles released during the use of various nanotechnology-based consumer sprays, cosmetic powders and nanotechnology-enabled clothing were examined. The use of these products was realistically simulated and it was found that nanosized particles as well as larger agglomerates would be released during the use of almost all investigated products. Number concentration of the released nanoparticles varied substantially depending on a particular product and product category. Some of the highest released nanoparticle concentrations were observed for spray products and reached concentrations as high as $10^6/cm^3$. Presence of Ag, Zn, Ti and other metals was observed in the released particles. For nanotechnology-enabled clothing, the release of particles was also observed; however the concentration of the released coarse particles decreased after the clothing items were washed.

Our results show that the use of investigated nanotechnology-enabled products would lead to inhalation exposure to nano-sized and larger particles. We estimate that the highest number of inhaled particles would deposit in the deep lung. A considerable amount (in some cases 80-90%) of inhaled particles in terms of their surface area and volume would deposit in the upper airways in the form of agglomerates. Future studies will address potential health effects due to exposures to particles from consumer products.

106B.2 Environmentally relevant exposures to nanomaterials in consumer products

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Outside of production and manufacturing, there are few opportunities for human or environmental exposure to neat nanoscale materials (NMs) stemming from use of articles containing them. Among the challenges to measuring exposure to

NMs in consumer products is the need to determine the exposure agent, a mixture of NMs in a matrix, and develop techniques for quantification in the matrix. Few reliable methods exist for capturing NMs at the receptor interface compounding well defined measurement challenges. For example, assessing exposure to particle based NM in a coating released from a textile during washing, while sweating, or with mouthing an object. There are many dimensions of exposure important in defining consumer use scenarios, including the relative importance of a particular exposure pathway, measurable criteria or categories, key transformations, use classifications such as frequency, duration, intentional/incidental, and cumulative exposures that inform selection of model and measurements. Examples of currently proposed approaches (EPA 2014; Sharma et al 2015 (not yet published); Collier et al (2015); and Shatkin et al. 2013) will be presented and discussed in the context of suitability and readiness for adoption.

106B.3 Characterization of mechanical and UV-induced nanoparticle release from commercial products

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Engineered nanomaterials (ENMs) are increasingly incorporated into commercial products to enhance their desired properties. For example, nanoSiO_2 and nanoAl_2O_3 in the flooring coatings provide improved wear resistance, nanoTiO_2 and nanoZnO in the exterior coatings and paints increase their ultraviolet (UV) resistance, and multiwalled carbon nanotubes (MWCNTs) are used to strengthen the composite materials in sports equipment. However, the increased use of ENMs in consumer products also increased the need to quantify and characterize potential nanomaterial release from these products during repeated exposure to mechanical stresses or damaging environmental conditions and assess the overall hazard associated with the use of nano-enabled consumer products.

This report will provide a brief overview of the recent NIST Nano Environmental, Health & Safety (nanoEHS) efforts and NIST/CPSC research on nanoparticle release from consumer products. Experimental and analytical approaches for detecting, capturing and quantifying released nanoparticles by abrasion and UV degradation will be presented. Some of the challenges associated the nanorelease sample collection and characterization processes will also be discussed. High resolution electron microcopy combined with energy dispersive X-ray spectrometry, laser scanning confocal microscopy (LSCM), and inductively-coupled plasma optical emission spectroscopy (ICP-OES) are some of the techniques employed to characterize released nanoparticles. High resolution electron microscopy provides the visual and elemental confirmation of nanoparticle species. Recent improvements in our automated imaging processes have enabled routine analysis of large sample area at nanoscale. Although LSCM does not have the spatial resolution of electron microscopy methods, LSCM combined with image analysis is a relatively fast and reliable screening method for assessing the abundance and size distribution of released metal oxide particles accumulated on abraded surfaces. ICP-OES is effectively used to evaluate the amount of silica released from the nano-enabled coatings through a NIST-developed simulated rain process or collected directly from surfaces of abraded samples and abrasion wheels.

106B.4 Quantifying the release of silver from nanotechnology-based consumer products for children

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We assessed the potential for children's exposure to bioavailable silver during the realistic use of selected nanotechnology-based consumer products (plush toy, fabric products, breast milk storage bags, sippy cups, cleaning products). All products had at least one component containing silver. Silver in particulate form was visible in the spray cleaning product, the interior foam and exterior fur of the teddy bear, the baby blanket, and in components of a sippy cup. Silver particles ranged from nanoscale up to 10 µm in size and appeared to be located on the surface and interior of fabric fibers and embedded in the components of the cup. We measured the release of ionic and particulate silver from products into water, orange juice, milk formula, synthetic saliva, sweat, and urine (1:50 product to liquid mass ratio); into air; and onto dermal wipes. Sweat and urine yielded the highest amount of released silver, up to 38% of the silver mass in products; tap water yielded the lowest amount, ≤1.5%. Leaching from a blanket into sweat plateaued within 5 min, with less silver released after washing. Between 0.3 and 23 µg m^{-2} of silver transferred from products to wipes. Aerosol concentrations were not significantly elevated during product use. Fabrics, a plush toy, and cleaning products were most likely to release silver. Silver leached mainly via dissolution and was facilitated in media with high salt concentrations. We predict that children may potentially be exposed to low concentrations of silver during the normal use of these consumer products, and bioavailable silver is expected to be in ionic rather than particulate form.

106C Consumer Exposure Studies II: Food, Food Contact and Personal Care Products

Shenandoah B

Co-Chairs: Timothy Duncan[1] and Margaret Kraeling[2]

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Selected topics in this session include potential exposure to nanocomposite food packaging, engineered nanomaterials used in consumer food and/or agricultural products (e.g., fresh produce), sunscreens, and cosmetics. Speakers will report on their efforts to investigate the potential routes of exposure (ingestion, skin absorption, etc.), to measure the quantity and morphology of ingested/absorbed particles, to develop methods to ensure relevant exposure data can be obtained, and to formulate and test predictive exposure models.

106C.1 Using dietary intake modeling to project human intake of nanomaterials present in agricultural foods and commercial products

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There is mounting evidence of environmental releases of engineered nanoparticles (ENPs). Evidence of the accumulation of ENPs in food crops has raised concern of possible risks to food safety. Those concerns for food safety are based almost solely on the supposition that accumulation of ENPs in plants represent an inherent risk. There is little tangible data that relates ENP accumulation in edible tissues to relevant dietary guidelines or limits that would place that ENP accumulation into an appropriate regulatory or risk context. Using data obtained from an accumulation study with carrot (*Daucus carota*) grown in the presence of either CuO and ZnO, or the ionic form of each, a series of age- and gender-specific dietary intake models were constructed. These dietary intake models projected the ingestion of Cu or Zn that would result from the consumption of fresh peeled or unpeeled carrot grown in the presence of the nanoparticle or ionic form of each element. The dietary intakes calculated for each class were compared to the oral reference

dose for chronic toxicity associated with each metal. The models indicated that dietary intake would be significantly higher for unpeeled carrots than for peeled carrots. The models also demonstrated that dietary intake of Cu or Zn would be significantly higher for those carrots grown with ionic Cu or Zn than for the nanoparticle treatments. Nevertheless, none of the models for nanoparticle-grown plants projected dietary exposures that would exceed the relevant oral reference dose. A reverse-modeling effort was conducted to determine the tissue concentrations or dietary consumption that would be needed to reach a dietary intake that exceeded the oral reference doses. A similar exercise was undertaken for several Ag nanoparticle containing nutritional supplements and the findings will be discussed. The approach here illustrates how dietary intake scenarios associated with a particular ENP and plant combination could be used to project the possible impact of ENPs in plant foods on human and consumers and the corresponding impact of ENPs on food safety.

106C.2 Challenges in the characterization of nanomaterials relevant to cosmetics and personal care products

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The state of exposure science and tools & methods available to characterize and quantify exposure are topics of central importance to the cosmetics and personal care products industry. This is due both to the essential role determining exposure plays in safety assessment but also because of the number of regulations which now include nano-specific obligations. The nanomaterial specific obligations for labeling and premarket notification in Europe under Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 is but one example where accurate characterization is critical to determining what is needed to conform with regulations.

The talk today will review several projects within the multilateral International Cooperation on Cosmetics Regulation (ICCR) initiative addressing the challenges faced in characterization of nanomaterials in cosmetics and personal care products.

106C.3 Studies on the potential of nanoparticles to migrate from polymer nanocomposites for food packaging

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The use of nanomaterials (NMs) as additives in food contact plastics is since some years an emerging field of research and development activities. The leading overall objective is to improve in this way the mechanical properties of food contact plastics needed to ensure food quality for longer shelf life times but also for manufacturing economy reasons. On the other hand, in analogy to usual conventional plastics additives, the question whether nanoparticles (NPs) can migrate from food contact plastics into a food was increasingly raised and investigated in numerous studies with diverging results and in a number of cases with speculative conclusions.

A frequently used nanocomposite system was nano silver particles (Ag-NPs) in food contact polyolefins because of the analytical ease to measure silver. However, to differentiate between nanoparticulate and ionic silver is not really an easy task.

Our lab has carried a number of migration studies on different polymer nanocomposites including a systematic study on nano silver, incorporated at different concentrations in low density polyethylene (LDPE) films in contact with food simulants according to European legislation. Detectable migration of total silver as measured by inductively coupled plasma mass spectrometry (ICP-MS) was found in aqueous food simulants only. Stability tests of Ag-NPs in these food simulants by asymmetric flow field-flow fractionation (AF4) analysis showed rapid oxidative dissolution of the Ag-NPs and demonstrated that only ionic silver was present in the migration solution. Non-detectability of silver both in the isooctane and 95 % ethanol migrates indicated that Ag-NPs would not be able to migrate. These findings were supported by a new approach of migration modeling showing that nanomaterials (NMs) in general are immobilized in a polymeric matrix, resulting in a very limited hypothetical potential for the migration of NMs smaller than 3-4 nanometer in diameter. However, such small nanoparticles are usually not found in polymer

nanocomposites. The results of all our studies suggest that migration of nanoparticles from food contact plastics cannot take place with the consequence that an exposure of the consumer from nanoparticles in food packaging plastics is very unlikely.

106C.4 Nanomaterial cosmetic research at the Food and Drug Administration

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The field of nanotechnology has continued to foster interest over the past ten years in manufacturing and regulatory spheres as a result of the potential unique properties as well as broad applications in a variety of settings, including cosmetics. During this time, the reports of nanotechnology-related consumer products, including cosmetics, have also increased and there has been continued interest in how these products should be assessed from a regulatory and a safety perspective. To address the information gaps, FDA has continued to support research in the areas of skin absorption of nanoparticles, including liposomes, dendrimers, and metallic oxides. Today's discussion will focus on the U.S. regulatory model and some ongoing research to assess the presence and the safety of nanotechnology in cosmetics.

106D Ecological and General Population Exposure Studies

Shenandoah C

Co-Chairs: Elijah Petersen[1] and Jeff Steevens[2]

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This session focuses on the emerging methods that address the challenges with characterizing exposure in the complex natural and built environment. These challenges include a wide range of matrices that have the potential to transform nanoparticles released into the environment and complicate an accurate characterization of relevant properties. Presentations will emphasize how these methods can be used to overcome these challenges to accurately assess availability and exposure.

106D.1 Accumulation and trophic transfer of engineered nanomaterials by plants

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Engineered nanomaterial (ENP) use in consumer products has expanded at a rapid pace but an understanding of the fate and effects of these materials has lagged behind. Nanomaterial use in agriculture is also increasing dramatically, with additional inputs to agro-ecosystems through ENP-containing biosolids. Although a robust literature on the toxicological interactions of ENP and plants is developing, the vast majority of the work is focused on short term, high dose exposure often under model conditions. This level of research was a necessary first step in the developing field of nanotoxicology but ultimately is not appropriately designed to answer the fundamental questions of exposure and potential hazard to food safety. In fact, our work is now driven by the central thesis that only long-term, low/realistic dose exposure of food crops to ENP under soil-based life cycle conditions will provide an accurate assessment of both receptor exposure and risk to food safety. This presentation will provide an overview of our recent studies on agricultural crop-ENP interactions, with a focus environmentally relevant exposure routes and conditions, interactions with co-existing contaminants that impact exposure, and on conditions that will influence ENP trophic transfer.

106D.2 A liquid nebulization / differential mobility analysis (LN/DMA) method for valid sizing and quantification of engineered nanoparticles in environmentally-relevant water matrices

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A liquid nebulization-differential mobility analysis (LN/DMA) methodology was evaluated for the measurement of the size distribution and quantitative number concentration of engineered nanoparticles (ENPs) in environmentally relevant aqueous matrices. The analysis time is eight minutes per analysis and requires little routine sample preparation and less than 8 mL of sample. For the ENPs studied, the method was capable of rapid, non-invasive, direct analysis of ENPs in many types of complicated aqueous media. Twelve NIST traceable reference materials consisting of polystyrene latex, SiO2, gold, and silver and having diameters from 18 nm to 200 nm were used in the evaluation. The reference materials were spiked into six aqueous matrices; algae and daphnia growth media used in ecotoxicology testing as well as semiconductor grade ultra pure water, groundwater-sourced drinking water, water used in manufacturing activities and an industrial wastewater. The mean measured particle diameters of the reference materials were within the expected NIST-traceable size range for the materials. Matrix matched calibration curves were prepared to determine the individual response factors of each reference material. The response factors were used to quantify the levels of the reference materials spiked into each aqueous matrix. For samples with appropriate signal to noise, and with the exception of one data point, recoveries were within the range of 70 to 130%. The method was used to collect samples onto TEM grid for further SEM and EDS analysis. Overall this method will be shown to be particularly well suited for dose verification in ecotoxicology studies as well monitoring emissions from manufacturing processes.

106D.3 Quantification of carbon nano materials in complex matrices

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Carbonaceous nanomaterials (NMs) are being developed in 1-D (single or multi wall nanotubes), 2-D (graphene sheets), and 3-D (C_{60} fullerene derivatives) and used in a wide range of applications from cosmetics to flame retardants and electronics. Assessing workplace and consumer exposures requires new interpretation of existing analytical platforms, and development of new methodologies to quantify each of these classes of carbonaceous NMs. This presentation discusses the commonly applied approaches, including HPLC-UV or LC-MS for C_{60} derivatives to thermal combustion processes adopted from airborne soot aerosol analyses for 1-D and 2-D nanomaterials. Other techniques ranging from single-particle ICP-MS of catalysts to Raman spectroscopy are summarized. A key challenge in these methods is specificity and accounting for functionalization or transformation in the NMs (e.g., oxygen functionality of the carbon). Solvent extraction methods have been developed for C_{60}, where it is treated more like a macromolecule than colloid. Alkaline and enzymatic digestion techniques allow for quantitative recovery and analysis of CNTs and graphene. A borohydrate based reduction technique for graphene is capable of removing oxygen influences on its thermal stability which are important for its quantification. Analysis of personal air monitoring devices show the ability to differentiate CNTs from background airborne soot. The presentation concludes with thoughts on future directions for exposure monitoring and instrument development needs related to carbonaceous NMs.

106D.4 An exploration of some capabilities and limitations of single particle ICP-MS

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Single particle ICP-MS (spICP-MS) is being advanced as a method for the characterization of metal and metalloid containing nanoparticles (NPs) at environmentally relevant concentrations in natural matrices. The method can be used for the direct analysis of aqueous suspensions of NPs and simultaneously provides information on size, size distribution, particle number concentration, aggregation state, and ionic content. However, before spICP-MS can be considered a mature methodology validation of the measurements and a robust exploration of error sources are required. This presentation will demonstrate the reproducibility and accuracy of spICP-MS for the measurement of particle size, particle size distribution and dissolved silver (Ag) content of NIST RM 8017 polyvinylpyrrolidone stabilized AgNPs with nominal diameter of 75 nm. To gain insight into error sources, we use a Kragten spreadsheet approach to combine uncertainty components to estimate the expanded uncertainty of the spICP-MS particle size measurement and to explore the influence of each error source. We demonstrate the utility of the method to characterize starting dose materials by using spICP-MS to measure the size and size distribution of gold (Au) NPs in several commercially available suspensions and then validate the spICP-MS results against high-resolution scanning electron microscopy (HR-SEM) measurements. Finally, we demonstrate the challenges encountered in the application of spICP-MS to the analysis of commercial textiles purported to contain a nano silver component.

Concurrent Session Abstracts

Wednesday

205A Exposure Studies in Gaseous Media

Shenandoah C

Co-Chairs: Vincent Castranova[1] and Gedi Mainelis[2]

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The goals of this session are to characterize airborne levels, size distribution and composition of nanoparticles generated during production and use of nanomaterials. The adverse biological responses to exposure to these nanoparticles will be evaluated and time course and dose-response described.

205A.1 Characterization of an aerosol generated during application of a nano-tio_2 enabled antimicrobial spray product to a surface: Pulmonary and cardiovascular response to inhalation exposure in rats

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Nanotechnology has progressed to a stage where nanoparticles are being incorporated increasingly into consumer products to enhance their functionality. To date, few studies exist, which report consumer exposure to nanoparticles aerosolized during use of nano-enabled products. The present investigation characterized user exposure during application of a commercial antimicrobial spray product containing nano titanium dioxide (TiO_2) onto a surface and determined the pulmonary and cardiovascular responses to inhalation of this generated aerosol in rats. Spray application of this product generated a total TiO_2 particle concentration of 3.4 mg/m^3 in the breathing zone of the user, with a mass median diameter of 345 nm and a count median diameter of 75 nm. The airborne concentration of nano TiO_2 was 0.17 mg/m^3 or 1.2 x 10^5 nanoparticles/cm^2. Inhalation exposure of rats to this aerosol at 3.79 mg/m^3, 4 hr/day, for 4 days (high dose) resulted in acute inflammation (increase of 109%), damage (increase of 50%), and an increase in breathing rate (7-8%). Inhalation to 9% (low dose) or 22% (mid dose) of this level caused no significant pulmonary response. Inhalation exposure at the high dose failed to alter the responsiveness of the tail artery to vaso-dilators or constrictors, indicating a lack of cardiovascular response. Risk analysis indicates that expected consumer use would result in an alveolar lung burden of TiO_2 below the NOEL in this rat study. (Supported by an Interagency Agreement between CPSC and NIOSH).

205A.2 Physico-chemical and toxicological characterization of engineered nanoparticles emitted from laser printers: A case study of consumer exposures across life cycle of nano-enabled products

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It has been recently demonstrated that Engineered nanomaterials (ENMs) incorporated into toner formulations of printing equipment become airborne during their consumer use. Although information on the complex physicochemical and toxicological properties of both toner powders and printer-emitted particles (PEPs) continues to grow, toxicological studies have primarily used raw toner

powders rather than the actual PEPs, which is not representative of current exposures experienced at the consumer level during printing. A multi-tiered methodology was designed to physicochemically, morphologically and toxicologically characterize the PEPs released from laser printers. A lab based printer exposure generation system (PEGS) suitable for the subsequent physico-chemical, morphological, and toxicological characterization of printer emitter particles (PEPs) was developed. PEGS was used to assess the properties of PEPs released from most commercially available printers. The system consists of a glovebox type environmental chamber for uninterrupted printer operation, real-time and time-integrated particle sampling instrumentation for size fractionation and sampling of PEPs. It also enables the direct exposure of animals for inhalation toxicological studies. Results from our extensive analysis show that laser printers emit up to 1.3 million particles/cm^3, with the majority by number to be in the nanoscale. Further, it was confirmed that PEPs possess a complex chemistry including organic and inorganic compounds. More importantly, a number of ENMs incorporated into toner formulations (*e.g.*, silica, alumina, titania, ceria, iron oxide, zinc oxide, copper oxide, carbon black among others) become airborne during printing. Both *in vitro* and *in vivo* toxicological evaluation showed PEPs are biologically reactive and may cause significant cytotoxicity, membrane integrity damage, reactive oxygen species production, pro-inflammatory cytokine release, angiogenesis, cytoskeletal and epigenetic changes as well as overall lung injury and inflammation. This work highlights the importance of understanding life-cycle specific environmental health and safety implications of nano-enabled products and assessing real world exposures and associated toxicological properties rather than focusing on properties of pristine ENMs used in NEP synthesis.

205A.3 Microvascular outcomes of engineered nanomaterial inhalation

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While the lung is the primary site of exposure, epidemiological evidence indicates the cardiovascular system is a principal site of impact. Many have initiated studies to evaluate the mechanisms linking pulmonary exposure with cardiovascular consequence. Traditionally, these studies have identified systemic microvascular endothelial dysfunction after engineered nanomaterial (ENM) exposure focused on young, healthy, male, occupational models.

As potential uses for ENM continue to develop, so does the risk of inevitable exposure within non-occupational settings and non-traditional models, including women of child-bearing age, expecting mothers and their unborn young. One of the most complex and acutely demanding circulations is the maternal-fetal coordination to support pup growth and development; these studies hypothesized female ENM exposure could influence uterine milieu, during would perturb the delicate microvascular balance during an otherwise healthy pregnancy, lead to the development of a hostile gestational environment, and impact fetal microvascular development.

Using *in situ* and isolated microvascular techniques, these studies evaluated agonist-stimulated endothelium-dependent, -independent, and vascular smooth muscle reactivity; results identified microvascular dysfunction at multiple levels of the vasculature, supporting the development of a hostile gestational environment and fetal impairments.

Collectively, this work indicates ENM exposure may lead to independent cardiovascular consequences of virgin females, pregnant mothers, developing fetus, and for the adult offspring exposed during gestation. These impairments may increase cardiovascular disease susceptibility and possible disturbances in conception for future generations.

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205A.4 Strategies for measuring airborne nanomaterials

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Airborne nanomaterials have the potential to impact environmental, public, and occupational health. As such, background and incidental airborne nanomaterials are ubiquitous in both developed and emerging countries. Furthermore, increased application of engineered nanomaterials (ENMs) in

consumer goods and research and development markets has led to a corresponding growth of nanomaterial-related manufacturing to meet this demand. As these sources are extremely diverse, opportunities for exposure to airborne nanomaterials are equally diverse. Environmental and occupational exposures to nanomaterials have the potential to be significant if not properly managed. However, evaluating and assessing potential exposure to airborne nanomaterials poses new challenges due to their small size, their negligible mass, and their high diffusivities. In addition to continuing questions regarding such issues as selection of appropriate dose metrics (mass, surface area, or number) and the identification of physico-chemical characteristics of nanomaterials that impact environmental and human health, sampling strategies may be necessary to identify any spatial and temporal changes in nanomaterial concentration and physico-chemical characteristics while also differentiating incidental and ENMs from background nanomaterials. Currently, exposure assessment and routine monitoring for airborne nanomaterials are either very minimal or non-existent. Whenever monitoring efforts occur, they do not generally follow any consistent strategy. However, strategies to conduct exposure assessments have begun to emerge. The goal of this presentation is to review sampling strategies and instrumentation characteristics needed to carry out exposure assessments for airborne nanomaterials.

205B Exposure Studies in Aqueous Media

Shenandoah A

Co-Chairs: Jeff Steevens[1] and Richard Zepp[2]

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Aqueous systems are an important phase in the release and exposure to nanoparticles. This session includes four presentations across the continuum of release from nanomaterial containing products in aqueous media, predicting fate and transport in the aquatic systems, and characterizing aqueous exposure. New approaches and techniques will be discussed that advance exposure science in this universal medium.

205B.1 Detection and release of carbon nanotubes from polymer nanocomposites

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Most engineered nanomaterials, such as carbon nanotubes (CNTs) will enter the environment within manufactured nanoproducts, such as polymer nanocomposites. Quantifying CNT release rates from nanocomposites is important not only from a life cycle perspective, but also in terms of risk assessment, because release is the necessary precursor to exposure. However, CNT detection in aqueous environments remains a major challenge due to the need to accurately detect and quantify CNTs in complex matrixes under conditions where CNT released concentrations are expected to be at part-per-trillion levels.

In the first part of my presentation I will review the existing methods available for detecting CNTs in aqueous environments, along with their strengths and weaknesses. These methods include TEM, UV-Vis, single particle-inductively coupled plasma mass spectrometry (spICPMS), thermal gravimetric methods and near infrared fluorescence. In particular, I will focus on the application of sp-ICPMS due to its extremely high sensitivity. However, due to the ambiguities inherent in detecting CNTs by carbon analysis, particularly in complex environmental matrices, we have been using sp-ICPMS to detect trace catalytic metal nanoparticles intercalated in the CNT structure as proxies for the nanotubes. Using a suite of commercially available CNTs, the monoisotopic elements Co and Y were found to be the most effective for differentiation of particulate pulses from background. The small amount of trace metal in each tube CNT makes

separation from instrumental background challenging; multiple cut-offs for determining CNT number concentration were investigated to maximize the number of CNTs detected and minimize the number of false positives in the blanks. In simple solutions the number of CNT pulses detected increased linearly with concentration in the ng/L range.

To test the suitability of this approach CNTs were embedded in polymers (e.g. chitosan, polystyrene) to create nanocomposites, which were then subjected to potential CNT release scenarios, including exposure to hydroxyl radicals and UV irradiation in aqueous environments. The resulting supernatants were sampled for spICPMS analysis and the presence of CNTs detected by monitoring residual metal catalysts such as Co, Y, and Mo. The presence of CNTs was found to significantly retard the rate of polymer photodegradation and lead to the steady accumulation of a CNT mesh at the surface. During the formation of this protective mesh at the surface, however, sp-ICPMS data suggests that CNTs are being released from the composite in concentrations that scale with the CNT loading in the polymer nanocomposite. As part of these studies, additional control experiments will also be necessary to ensure that the metals remain attached to the carbon nanotube during the release process. These results highlight both the progress, but also the significant experimental challenges that still remain in quantifying exposure to engineered nanomaterials (QEEN) from manufactured products.

205B.2 Simulating the fate and transport of nanomaterials in surface waters

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The unique properties of nanomaterials have resulted in their increased production. However, it is unclear how nanomaterials will move and react once released to the environment One approach for addressing possible exposure of nanomaterials in surface waters is by using numerical, mechanistic fate and transport models. The currently available environmental fate models that have been developed for traditional contaminants are limited in their ability to simulate nanomaterial behavior in the environment. We are currently redesigning WASP to incorporate nanomaterials as a state variable and incorporating algorithms to address the processes governing nanomaterials in aqueous media. This presentation will discuss the processes necessary to simulate nanomaterials in surface waters, the processes being incorporated into the updated WASP, how the updated WASP will compare to the current WASP, and the projected studies and simulations to investigate how nanomaterials move through surface waters.

205B.3 Understanding and quantifying nanomaterial exposure and dosimetry in aquatic hazard testing - The link between hazard, exposure, and risk assessment

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Many of the technical issues that are essential for understanding environmental nanomaterial exposure in natural aquatic systems are equally critical in the controlled aquatic assays used in regulatory testing. Exposure-response values derived from regulatory-level assays provide the basis for the hazard x exposure = risk equation. In these assays, insufficient exposure quantification can contribute to uncertainties in hazard estimation and ultimately in assessing risk from manufactured nanomaterials. Nanomaterials in aquatic toxicity test systems typically agglomerate and settle from test media, release dissolved substances (e.g. silver, zinc, and copper NP), and undergo modifications or transformations. In the majority of reported hazard studies, these behaviors and processes are not quantified, and in some cases not recognized or acknowledged. Exposure-response estimations are commonly based on nominal values, and typically limited to mass concentration-based dosimetry. In recent preliminary studies involving exposure of *Ceriodaphnia dubia* to nano-TiO_2, we found measured material water-column losses over 4 hours ranging from 1.4 % to 86% across a range of initial exposure concentrations ranging from 2 to 7 mg TiO_2/ L. Losses were also found to vary with

initial concentration. In addition, concentrations of TiO_2 were below reporting limits after 48 h at all target exposure levels. Exposure variability is further complicated for soluble nanomaterials, where dissolution increases exposure to soluble constituents while agglomeration and settling reduce particle exposure. For example, we have measured increases of dissolved silver from below detection limits to levels (0.8, 1.2, 1.8 ug Ag/L) sufficient to cause toxicity in *C. dubia* over a 48 h period. In the TiO_2 example, dosimetry based on nominal values would clearly (and potentially, significantly) underestimate hazard. These examples suggest that exposure estimation could be improved by the use of time-weighted averages, geometric mean, or other approaches to estimating exposure-response values. Exposure metrics other than mass concentration, including particle and aggregate/agglomerate size distribution and number, and surface area may be important and also vary significantly in controlled assay conditions. Additional examples will be used to illustrate exposure variability and to discuss factors that influence exposure and levels of uncertainty introduced by inadequate dosimetry. Finally, the link between environmental modifying factors (e.g. sunlight and dissolved organic matter) that can strongly effect exposure-response will also be discussed.

205B.4 Assessing nanoparticle migration from commercial food contact materials into aqueous food simulants

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It is widely accepted that there are a great variety of potential uses of nanotechnology in the food sector. Currently there are only limited applications, with a majority of these early uses being in the area of food contact materials (FCM). The most widely used material, silver nanoparticles, has been incorporated into a variety of products, often with the intention of reducing bacterial growth and maintaining the "freshness" of food.

Characterizing the commercial products, including the physico-chemical properties and potential migration of constituents (traditional and nano-forms) is an important step in assessing the safety of FCMs. Methods for characterizing traditional FCMs are well established and validated, however the applicability of these methods to nano-containing FCMs
has not been widely studied. Additionally, the characterization of nanoparticles requires methodology (electron microscopy, particle sizing) not generally utilized with traditional FCMs. The goal of this project is to identify/develop methods for characterizing nanomaterials used in food contact applications and to evaluate the applicability of conventional migration protocols to the nano-products. Along with presenting data of the migration of nano-Ag from commercial FCMs, the talk will also discuss methods for assessing the conflicting reports regarding nanoparticle migration into food simulants.

205C Exposure Studies in Biological/Tissue/Serum

Shenandoah B

Co-Chairs: Will Boyes[1] and Elijah Petersen [2]

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This session focuses on the emerging methods that address the challenges with characterizing exposure in organism tissues and biological media such as serum. These complex matrices can complicate engineered nanomaterial quantification. Presentations will highlight methods for quantifying engineered nanomaterials and nanomaterial transformations in these matrices.

205C.1 Assessment of the bioaccessibility of micronized copper wood in synthetic stomach fluid

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The widespread use of copper in treated lumber may result in a potential for human exposure. Due to a lack of information concerning the release of copper from treated wood particles following oral ingestion, the *in vitro* bioaccessibility of copper from copper-treated wood dust in synthetic stomach fluid (SSF) and DI water was investigated. Copper-containing particles ranging in size from nano-scale to micron-scale were observed by Transmission Electron Microscopy (TEM) in thin sections of these micronized copper-treated wood products. Three copper-treated wood products (liquid alkali copper quaternary and two micronized copper quarternary products) from different manufacturers were incubated in the extraction media. The released copper was then fractionated by centrifugation and filtration through 0.45 μm and 10 kDa filters, respectively. Soluble copper released into isolated fractions was measured using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Total copper from each wood product was also determined using microwave-assisted acid digestion of dried wood samples and ICP-OES. The bioaccessible copper released into SSF was between 83 and 90% for all wood types. However, the percent of copper released in DI water was between 14 and 25% for all wood products. These data suggest that copper is highly bioaccessible at the low pH values present in the stomach and may pose a potential exposure risk upon ingestion.

205C.2 Using single particle ICP-MS as a tool for understanding metallonanoparticles transformation during nanotoxicity assays

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The advent of engineered nanoparticles (ENPs) has remarkably improved the performance of basic materials and consumer products, leading to the commercial success of ENPs and a rapid rise of the nanotechnology industry. Presently, there is an urgent need to understand how ENPs interact with environmental and biological systems. While several analytical methods have been developed to quantitatively study complex systems, techniques developed for macro-scale physical and chemical properties are not well suited for ENPs. There is a need for techniques that are more analytically sensitive (in regards to environmentally relevant concentrations) than conventional approaches (e.g. TEM, SEM, DLS used for nanoparticle characterization and quantification). Single particle inductively coupled plasma-mass spectrometry, spICP-MS, has emerged as a technique potentially capable of measuring ENPs in complex matrices (after suitable extraction) at the pg/L range. The work presented combines spICP-MS, density gradient separation, and acid and base digestions to measure the uptake of metallonanoparticles into a model organism, *Caenorhabditis elegans*. A spICP-MS method was validated for sizing Au ENPs using well-characterized reference material (RM) ENPs (NIST RM 8012 and 8013; 30 nm and 60 nm Au ENPs, respectively). *C. elegans* populations were exposed to the Au ENPs in liquid media for 24 h. Common washing procedures were ineffective at removing excess suspended Au ENPs after exposure. Therefore, a sucrose density gradient centrifugation protocol was optimized and employed to separate the nematodes from Au ENPs freely suspended in the exposure media. Quantification of total Au uptake in dry samples of control and Au exposed *C. elegans* was determined following acid digestions (for conventional ICP-MS analyses) and alkaline

digestions of biological tissue (for particle sizing in spICP-MS analyses). Nanoparticulate body burdens were measured for each Au ENP uptake condition. Finally, size distributions and particle number concentrations were determined for all ENPs dispersed in water, ENPs dispersed in exposure media, and ENPs taken up by *C. elegans*. Our results suggest that accumulation of Au ENPs in *C. elegans* can influence the size distribution of the ENPs, which may be a result of the ENPs being exposed to physiological processes (i.e. gut compaction) within the nematode.

205C.3 Measuring exposure levels of drug products containing nanomaterials

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In recent years there has been an increased focus on developing novel drug delivery systems through the use of nanotechnology and nanomaterials. With this increased focus, there has been a corresponding increase in applications for drug products containing nanomaterials to the United States Food and Drug Administration (FDA) submitted for Agency review. Although subject to the same rigorous regulatory standards as any other drug product, unique properties that arise from the small size and large surface area of nanomaterials may lead to additional scientific considerations when following current FDA guidelines and practices. Such considerations may extend to determining the extent of exposure and distribution of a nanomaterial within the body once administered. This presentation will discuss these scientific considerations and present current regulatory research efforts to address nanomaterial exposure evaluation in biological tissues.

205C.4 Determination of the fate of inhaled nanoparticles

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A number of approaches can be employed to assess the health risks from inhaled engineered nanomaterials. Our research has focused on identifying potential critical target site(s) by using newly developed microscopic imaging techniques to detect individual nanoparticles in the lungs and follow the transport of nanoparticles that are potentially transported to other organs. This presentation will discuss our use of this method in the study of inhaled mutli-walled carbon nanotubes (MWCNT) in the mouse. The mouse inhalation was a whole-body inhalation exposure with 5 mg/m^3 MWCNT aerosol for 5 hours/day for 12 days (4 times/week for 3 weeks). The distribution of MWCNT was determined in the lungs, tracheobronchial lymph nodes draining the lungs, the parietal pleura, respiratory musculature and systemic organs at 1 day, 14 days, 168 days and 336 days after the 12 day exposure period. Enhanced darkfield microscopy and morphometric methods were used to detect and count MWCNT in tissue sections. Field emission scanning electron microscopy (FESEM) was also used to examine details of MWCNT structure in the various tissues. Tracheobronchial lymph nodes were found to contain 1.08 and 7.34 percent of the initial lung burden at 1 day and 336 days post-exposure, respectively. Although agglomerates account for approximately 54% of the burden in the lungs, only singlet MWCNT were observed in the diaphragm, chest wall, liver, kidney, heart and brain. On average, there were 15,371 and 109,885 fibers per gram in liver, kidney, heart and brain at 1 day and 336 days post-exposure, respectively. The burden of singlet MWCNT in the lymph nodes, diaphragm, chest wall and extrapulmonary organs at 336 days post-exposure was significantly higher than at 1 day post-exposure. Results demonstrate that inhaled MWCNT, which deposit in the lungs, are transported to the parietal pleura, the respiratory musculature and the systemic organs in a singlet form and chronically accumulate in systemic organs following exposure.

205D Epidemiology: The Exposure-Health Interface

Dogwood

Co-Chairs: Mary Schubauer-Berigan[1] and Sara Brenner[2]

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This session will feature researchers conducting state-of-the-science studies of exposure and associated measures or indicators of possible early health effects among workers and others exposed to engineered nanomaterials. It is anticipated that this session will raise awareness among other disciplines of the importance of incorporating appropriate physical, chemical, and route-of-exposure metrics to studies of health effects in those exposed to engineered nanomaterials, and will identify research needed to correlate exposure data and health effects.

205D.1 Nanodermatology: Identifying promise and assessing risk

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Nanotechnology is a burgeoning field with tremendous potential for society and medicine. Over the past decade, it has entered an exponential growth phase in the number and variety of products soon to be or already available for consumers and patients. Today, nanotechnologies are being employed predominantly as nanomaterials, as opposed to nano-machines or –computers, in sunscreens, emollients, soap, shampoo, lipstick, eye shadow, after shave products, deodorants, and anti-aging products. Here, they potentially offer several advantages as vehicles for topical delivery, overcoming issues of penetration, dosing, and controlled delivery of bioactive agents. While there are many advantages to utilizing nanomaterials, specifically with respect to cutaneous drug delivery, the proliferation of nanomaterials in skin care products, the environment, and the workplace has brought legitimate concerns to the forefront. Given the skin is the first line of defense, and the first point of contact for the majority of nanomaterials, there is considerable interest in cutaneous penetration and resulting biological impact. The potential for nanomaterials to penetrate intact skin in animal models and human ex vivo models has been shown in these preclinical models - penetration that can be enhanced with certain vehicles, with flexion of the skin, and in damaged skin. However there is an equal share of studies demonstrating that commercially available nano-products do not in fact overcome the cutaneous barrier. In this lecture, I will review the biology of the skin barrier as a basis for the utilization of nanotechnology in dermatology, discuss how and where nanotechnology is already being employed in this clinical space, and conclude with the benefits and limitations of current techniques used to evaluate cutaneous penetration and toxicity from exposure.

205D.2 Epidemiologic studies of U.S. workers handling carbon nanotubes: The interface between exposure and health

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Workers are typically the first to encounter potentially toxic materials, such as engineered nanomaterials (ENM) and other advanced materials. Information from epidemiologic studies of possible health effects from exposures among workers can be valuable in elucidating the potential human impacts of exposure. This presentation will describe the approach used by researchers from the National Institute for Occupational Safety and Health (NIOSH) to prioritize exposure and epidemiologic studies of workers exposed to a major class of ENM: engineered carbonaceous nanomaterials. In particular, challenges associated with accurate characterization of exposure will be described.

205D.3 Field-based exposure assessment: Tailoring your approach to maximize and obtain key data for each worker

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Dr. Brenner will discuss exposure assessment methodologies and sampling strategies that are

currently used in field-based studies, their strengths and practical limitations, and how the data generated may or may not contribute to our understanding of health effects. The relationship of exposure data, hazard or toxicologic data, and epidemiology will be discussed with a focus on where knowledge gaps currently exist and how researchers in different disciplines can work together to design research strategies that contribute to our understanding of the "big picture" of population health.

Poster Abstracts

108.01 Nanotech for waste minimization

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The SAFE Foundation has currently been developing a systematic research strategy devoted to the careful examination of the Nanotech (NT) products and services for environmental protection and cleanup that is focused on potential applications facilitating waste minimization. The current ad hoc approach by the U.S. EPA has already resulted in the publication of a Fact Sheet with snapshots of the current usage of NTs in certain selected waste site remediation projects (USEPA, 2008). Though much of the NT processes are just entering commercialization or are under development, it may be evolving quite rapidly and holds much promise for the cost-effective remediation of the challenging waste sites, as per recent U. S. EPA and other research reports.

This paper reviews some waste treatment options using selected NT products and services that were found to be effective and also determined to be quite mature. The analyses of nanotechnology based processes for contaminant reduction and contaminant degradation by way of utilizing certain NPs like nZVI, coated nZVI, modified nZVI, bi-metallic nZVI, $nTiO_2$, and nZnO also indicate that significant waste minimization objectives may be achieved in the short and the long run by these carefully selected processes.

However, more detailed study of the environmental fate of all NPs, released at disposal, should be made an integral part of every NT waste treatment project, as detailed by Breggin and Pendergrass (2007). Besides, every effort should be made to remove NPs from the waste stream by way of proper adsorption, encapsulation, filtration, and suitable "end of pipe" treatment prior to disposal. These processes have been discussed elsewhere (Chatterjee and Lewinski, 2009) and will also be presented in future publications.

An overview of the technological developments to date shows that a vigorous pursuit of the desired source reduction practices are expected to ultimately achieve a more broad based NT-facilitated effective hazardous waste management some years down the road.

108.02 SERENADE An 8 year French funding safe(r) by design project. Introducing consumer exposure case studies

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Nanotechnology appears as one of the most promising fields of science and technology. The improvements and modifications of these new nano scale materials properties can appear disruptive and strongly challenges the existing products and technologies. In most cases nanotechnologies will bring beneficial effects in our lives (medicine, environment, electronics…). Nanotechnology therefore appears as strategic and a key of success in the globalized economy. However the fast development of nanomaterials and the estimated production for next years has triggered many debates concerning their safe development and use.

To reach the forecasted level of economical development, the public acceptance of nanotechnology is essential not only in terms of human health safety but also concerning the environmental impact. Nanotechnology faces a big challenge that requires to develop a new paradigm in the concepts of design and production of nanomaterials.

The project SERENADE (funded by the French National research Agency (ANR – LABEX call)

proposes an integrated scientific and educational approach to develop new concepts and tools for the Safer and Ecological Design in Nanomanufacturing Processes and Products. It is supported by a French national multi-disciplinary network of 14 academic partners including most of the French pioneering groups in the field from fundamental to applied research (Aix-Marseille University, CNRS, CEA, INSERM, INERIS, INRA,…) and education (Higher Education Pole (PRES) Aix-Marseille University, University Joseph Fourier, Montpellier University, University Paris-Est-Creteil, Novancia Business School, etc…) and 2 industrial partners (Suez-Environment, ALLIOS).

To reach this ambitious objective the core of the project will be structured around the three stages of the life cycle of nanomaterials: 1) Production 2) Usage 3) End-of-life and consumer case studies. The aim of the presentation is to introduce the different cases studies from cosmetics, paints, food packaging, nano-wire based products, and with a specific focus on the determination of consumer exposure.

108.03 Quantifying toxicity levels of engineered silica nanoparticles used in semiconductor manufacturing

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With rapid developments in the use of engineered nanoparticles (ENPs) in various fields such as in consumer goods, medicine, energy, information technology and in packaging, the impact of workplace and environmental exposure is not been thoroughly understood. In particular, the ENPs of silica, ceria and alumina are used in large quantities in polishing slurries for a semiconductor manufacturing process called Chemical Mechanical Planarization (CMP) of silicon wafers. For example, about 2.4 million metric tons of silica NPs was used in 2014 by the semiconductor industry (Holden et al., 2014). However, the regulations for use and toxic levels for these ENP slurries are yet to be established. Therefore, it is very important to study the ESH impact of silica NPs and subsequently establish safe threshold limits. The objective of this work is to quantity and correlate worker exposure/environmental discharge levels and threshold limits of toxicity for silica nanoparticle slurries to their physicochemical properties before and after the CMP process. The threshold limit of toxicity is formulated by calculating the half maximal inhibitory concentration (IC50). IC50 value is a measure that represents the effectiveness of a substance in inhibiting 50% of specific biological/biochemical function. In the current study, we will present a time-dependent toxicity and threshold limit comparison between pre- and post-CMP slurries containing colloidal silica ENPs after polishing semiconductor patterned test wafers of high-density plasma (HDP) oxide (MIT 864) on high-volume manufacturing IPEC Avanti 472 CMP tool. In addition, we will also present comprehensive characterization of pre-CMP slurries and post-CMP waste using a host of physicochemical techniques such as DLS, zeta potential, BET, XRD, FTIR, Raman, SEM and TEM. Lastly, we studied time- and dose-dependent impact of pre slurries and post-waste on lung epithelial cells (A549 lung epithetical cell lines) for 6-48 hours to determine IC50 for cytotoxicity (cell viability and membrane integrity). It was clearly observed that colloidal and fumed silica ENPs in slurries exhibited dose- and time-dependent IC50 for cytotoxicity.

108.04 A nano-architectured electrode for a high-performance supercapacitor

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There is an emerging need for improved electrical energy storage devices. This project aims to develop a robust electrochemical capacitor (supercapacitor) electrode with high energy density, long life cycles and a wide range of operational temperature. We take advantage of a low-cost, high conductivity, mechanically flexible mat consisting of electrospun

carbon nanofibers (ECNFs), coupled with skills for a high dielectric, uniform coating to produce a state-of-the-art supercapacitor electrode with superior performance. Preliminary results represented by the cyclic voltammograms (CVs) obtained from the MnO_2 coated ECNFs electrodes in 6 M KOH aqueous electrolyte gave a capacitance of 1247 F/g at current density 117 A/g. Furthermore the ECNFs mats electrode present excellent cyclic stability. The planned major work will be the introduction of uniform nano-architectured high-k materials to the ECNFs electrode via various techniques to enhance the energy storage density and power density.

108.05 Silver nanoparticle release from commercial plastic articles

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Silver nanoparticles (AgNPs) are used for wide range of applications due to their antimicrobial activity, including personal care products, appliances and different household items. In the recent years, the number of consumer products containing AgNPs has increased. While there is a lot of research focusing on effects exerted by nanoparticles, the knowledge concerning release and exposure to nanoparticles is very limited.

To investigate whether AgNPs can be released from plastic articles and consequently lead to consumer exposure, we tested four brands of commercially available plastic food containers and two brands of toothbrushes that advertised the presence of AgNPs. The release rates from food storage containers were performed following European Commission Directive 97/48/EC for articles intended to be in contact with food. Experimental setup involved incubating products for 10 days at 40°C with three different food simulants (Milli-Q water, 10% ethanol, and 3% acetic acid). The release of silver from toothbrushes was assessed by mixing toothbrushes in tap water for 24h at room temperature. The total amount of silver in selected products and migration solutions was quantified by ICP-MS analysis, and the size of the migrated particles was investigated by single particle ICP-MS (spICP-MS) and TEM imaging coupled with EDS.

The results showed that AgNPs were indeed present in the plastic articles and had the potential to migrate from the food storage containers as well as from the toothbrushes. The highest release rates from food storage containers were measured in 3% acetic acid. The size of released particles ranged from around 10 to more than 200 nm in diameter (by TEM-EDS). AgNPs released from toothbrushes were mostly in the size range of 40-60 nm in diameter (by spICP-MS), but no Ag particles were found by TEM imaging.

This work emphasizes that consumers can be exposed to AgNPs by using commercially available AgNP-containing products. This kind of data can assist in consumer exposure assessment which could subsequently aid appropriate human risk assessment and labelling of products containing NPs.

108.06 Testing strategy to measure exposure throughout the life cycle

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To address the concerns about the risks associated with nanotechnologies, regulations agencies are seeking tools for reliable and efficient decision making. While considerable efforts are undertaken to characterize possible hazards, the exposure to nanomaterials over the entire life cycle still remains a somewhat neglected research domain. However, meaningful risk assessment requires a reliable high-quality characterization of the exposure.

The EU project NanoReg addresses this issue in a regulatory approach. The work package "Exposure through Life Cycle Analysis" aims at:

- Characterizing real exposures (intensity and frequency) to humans (workers and consumers) and the environment during the entire life cycle of nanomaterials.
- Providing companies and legislators with a set of tools for risk assessment and decision making for the short to medium-term, by gathering data

and performing pilot risk assessment, including exposure monitoring and control, for a selected number of manufactured nanomaterials (MNMs) used in products.

- Developing, for the long-term, new testing strategies adapted to a high number of MNMs for many factors susceptible to affect their environmental and health impact.

The various tasks in this work include identifying high release scenarios and data gaps; characterize nanomaterial release qualitively and quantitatively with harmonized testing procedures relevant to all stages of the life cycle; develop predictive exposure models; assess risk management measures.

This paper shows how the work developed within the NanoReg project addresses major knowledge gaps in the exposure assessment.

108.07 Release of copper nanoparticles from pressure-treated lumber through simulated dermal contact

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Micronized copper pressure-treated lumber has become the dominant product of the consumer lumber treatment industry. The micronized treatment formulation contains copper carbonate ($Cu_2CO_3(OH)_2$) particles ranging in size from a few nanometers to several microns. The present research investigated the release of copper from consumer lumber products during simulated dermal contact and if the copper released was in a particulate form. Treated lumber was purchased from retailers and left to weather outdoors for approximately one year. Wipe samples were collected at time 0, 14, 34, 70, 97, 140, 260, and 399 days. The two as-purchased micronized copper materials were analyzed via XAFS and SEM and determined to contain copper carbonate particles with sizes of, on average, 121 x 56 and 244 x 105 nm (L x W), respectively, with a large fraction of the particles below 100 nm in at least one dimension. Surface wipe samples were analyzed for total copper and revealed a high initial release of copper that became constant (~1.5 mg m^{-2}) after one month. Copper particles were identified on the sampling cloths during the first two months of the experiment, after which the levels of copper were insufficient to collect data. The XAFS and SEM data showed that particles were always associated with cellulose material, indicating that they were released with dislodged wood material and not as free particles.

108.08 Development of a sensitive assay to detect and characterize the effects of nanomaterials on aquatic ecosystems using an *ex vivo* preparation of crustacean olfactory receptor neurons

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As the use of nanomaterials in all industries increases, the impact of nanomaterials on the environment must be understood. While much progress has been made in determining end-point toxicity (i.e., EC_{50}'s etc.), very little effort has been made to understand the myriad other interactions of nanomaterials with animals in the environment. While overall toxicity is important, there is a paucity of information about the effects of nanomaterials on behaviors such as foraging, mate selection, migration and predator avoidance. Many of these behaviors rely on sensing chemical cues from the environment, however it is unclear how nanomaterials affect these behaviors. In many ways nanomaterials are desirable because their small size give them unique chemical and physical properties. This small size, however, makes them somewhat problematic to certain ecosystems. In particular, the

tendency of colloidal nanomaterials to agglomerate and fall out of solution in aquatic environments means they often aggregate in sedimentary ecosystems.

In order to investigate the possible effects of nanomaterials on sedimentary ecosystems, we have developed an assay to measure the potency of nanomaterials (e.g. carbon nanotubes, fullerenes, quantum dots, etc. in their natural colloidal state in water) as olfactory stimuli for various commercially and ecologically important crustacean species. Crustacean olfaction relies on groups of Olfactory Receptor Neurons (ORN's) arranged in clusters and housed in cuticular extensions called aesthetascs found on two, paired antennae. It has been previously shown that the magnitude of stimulation of these neurons in response to stimuli is indicative of the attractive or repulsive nature of the stimulus. We hypothesize that nanomaterials in environmental mediums will stimulate ORN signaling pathways, which will allow for the precise and quantitative assessment of their exposure to crustacean species. To test this hypothesis, primary ORN from antenna are challenged with a wide range of nanomaterials at different concentrations and intracellular release of calcium measured using fluorescent dyes, a flow chamber, and confocal microscopy. This research is of great importance as there are currently no established assays to assess the ability of nanomaterials to stimulate and alter signaling pathways in crustaceans, which may be predictive of detrimental behavioral consequences of exposure.

108.09 Release of silver nanoparticles from nano-enabled water treatment membranes across the product's life cycle

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In recent years progress has been made in the development of nano-enabled polymer membranes for water treatment; giving way to the designing of next generation membranes with high performance and antifouling properties. Many studies note the potential added benefit of incorporating nanosilver into water purification applications, and point-of-use products are currently available for purchase. The potential affects of leached nanomaterials to the environment illuminate the need to forecast exposures in support of future risk assessments. Here we aim to help address this research need by quantifying release under varying use and disposal scenarios. This research explores the roles of polymer type, membrane pore size, and dissolution matrix in the release and dissolution of silver nanoparticles from nano-enabled membranes. In doing so we (1) synthesize and characterize several types of polymer membranes impregnated with Tween-20 nanoparticles, (2) perform passive release experiments designed to mimic the potential material and chemical stresses subjected to the product during the use and disposal phases of its life cycle, (3) and assess efficacy by testing the antibacterial properties of the membranes.

108.10 Physical-chemical state and mechanisms of nanomaterial release from products during their life cycle: Self-cleaning cement and acrylic wood coating case studies

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The industrial scale production and wide variety of applications of manufactured nanomaterials (NMs) and their possible release into the natural aquatic environment have produced an increasing concern among the nanotechnology and environmental science community. Even if a large piece of data is dedicated to address hazard of NMs few data exist on the exposure side, the second essential aspect of risk assessment. Environmental and consumer exposures will be based on many possible abiotic and biotic processes affecting stability (bio-degradation), fate, transport, and transformation of released nanomaterials. Moreover as function of the different stages of life cycle of product incorporating NMs, the structure, shape and properties of released NMs will vary. The study of nanomaterial releases from solid matrices (in which NMs are incorporated) is therefore an emerging field of research. Until now most efforts have focused on quantifying and identifying the released objects, providing valuable inputs to risk assessment models. However the mechanisms lying behind release are still largely unknown and rarely investigated. Nanomaterials are used in construction to improve the properties and functions of commonly used building materials like cements, glasses, paints etc. A part of this production concerns a new type of cement, called self-cleaning cement which maintains clean and white wall fronts. Such building materials may also provide interesting pollution-reducing properties. Nanomaterials have also wide applications in paint and coating industry. They can improve rheological and mechanical properties of the products, confer them self-cleaning or antimicrobial capacity, or act as UV-absorber, stabilizing agents, pigments, etc.

Along their life cycle cements and especially the use stage, paints and wood coatings will however experience processes that may lead to NOAA (Nano-objects, their aggregates and agglomerates) release. This is especially true for outdoor products, as sunlight and rain can induce very strong degradations. The aim of this study is to determine the mechanisms of NOAA release for two case studies: self-cleaning cement, and wood coating, incorporating TiO2-based and CeO2-based NMs respectively, during aging process and to identify parameters controlling it. Specific aging and weathering protocols were developed at the CEREGE to mimic at best products uses and environmental and consumer exposures. The elements released (particulate and soluble fractions) and their kinetic were quantified using separation techniques and chemical analysis (ICP-OES/MS) and characterized with DLS and TEM. We thoroughly analysed the aged solid matrices (from unaltered core to surface altered layer) using laser-ablation-ICP-MS and several X-ray based techniques: XRD (X-Ray Diffraction), µ-XRF (micro X-Ray Spectroscopy) and an unprecedented combination of nano and micro X-ray computed tomography to perform a complete altered matrix characterization including pore structure. Original results concerning the low-stability of the matrices while NOAA are released in fresh water will be detailed with regards to the size and surface properties of nanomaterials (nano-TiO2 in cements and nano-CeO2 in wood coatings). Moreover a deep investigation of the alteration mechanisms of cement and wood coatings will help deciphering which physical and chemical properties control NOAA release. Based on our results a predictive strategy will be proposed.

108.11 Toxicological comparison of *in vitro* exposure techniques of commercial nano products to lung cells

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Engineered nanomaterials (ENMs) are widely claimed as an ingredient in various products, including medicines, cosmetics, and cleaners. Historically, this claim has proven false for some nano-labeled products and even harmful to consumers who have been exposed to aerosols generated through proper use. Unlike medicines, manufacturers of consumer products are responsible for ensuring their products are safe but are not required to provide documentation. By investigating the specific toxicological effects of ENM containing consumer products to the lungs using *in vitro* models, we can better screen for potential immediate effects to the human body from commercial use.

Two commercial products, Mesocopper (Purest Colloids, Inc.) and Superior Nanowax (Eagle One), were characterized by dynamic light scattering and transmission electron microscopy and exposed to multiple lung cell lines. Each of these products was chosen from the Woodrow Wilson Center's

Consumer Products Inventory list of products with manufacturer claims that the product include EMNs but has no documentation providing support of the claim. Mesocopper is a colloidal suspension of copper nanoparticles used as a mineral supplement with claims such as promoting healthy skin, promoting metabolism of specific neurotransmitters, and helping with tendon regeneration [1]. Nano-sized carnauba particles are used to promote shine, reduce dust, and repel water from one's vehicle in the use of Superior Nanowax [2]. Both products are aerosolized during use and thus inhalation is a concern. The lung cells used were the A549 alveolar adenocarcinomic epithelial, the BEAS-2B immortalized normal bronchial epithelial, and the Calu-3 bronchial adenocarcinomic epithelial cell lines. Suspensions and air-liquid interface exposures, where the cells are grown on a membrane exposing one side to air, were used to expose the cells to the product aerosols and compare the cytotoxic and oxidative stress responses.

[1] www.purestcolloids.com/mesocopper.php
[2] www.eagleone.com/superior-nanowax-spray

108.12 Nano-waste: Environmental health and safety implications during thermal degradation/ incineration of nano-enabled products at their end-of-life

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Engineered nanomaterials (ENMs) are increasingly being incorporated into consumer products such as car tires, paints, toners for printing equipment, building materials and cosmetics, to name a few. This exponential proliferation of nano-enabled products (NEPs) in the consumer market has rendered human exposure to ENMs released across life cycle of NEPs inevitable. Over the past decade, the risk assessment paradigm for nanomaterials has focused primarily on potential adverse effects of pristine (raw) ENMs. However, the physicochemical properties of ENMs may be drastically altered across their life-cycle, especially when they are embedded in various NEP matrices. There is limited understanding on the release mechanisms and properties of released particles throughout the NEP life span which may or may not contain the ENMs used in its synthesis.

The end-of-life scenario of NEPs through thermal decomposition is of particular interest and raises concerns of a possible emerging nano-waste problem from the resulting byproducts of such a process. Recent studies on the material flows of ENMs through society indicate that 60-80% of all ENMs end up in landfills and approximately 9,000 metric tons/year end up in incineration facilities. Additionally the use of ENMs in building materials and furnishings raises concerns on the implications of incidental fires in the built environment.

Here, we systematically investigate the thermal decomposition of one of the most widely used industry-relevant family of NEPs, namely, thermoplastic polymer nanocomposites enabled with a variety of organic and inorganic nanofillers using a recently developed standardized, versatile and reproducible integrated exposure generation system (INEXS), that allows for the systematic physicochemical and toxicological characterization of the thermal decomposition of NEPs. The target of the study is to establish a fundamental understanding of the parameters that govern the thermal decomposition of NEPs and affect the physicochemical properties of the byproducts (released aerosol and residual ash).

Our results indicate that thermoplastic polymer matrix strongly influences the size and morphology of the released aerosol, while there is minimal but detectable nano-release, especially when inorganic nanofillers are used. The chemical composition of the released aerosol was found not to be strongly influenced by the presence of nanofiller at least for the low, industry-relevant loadings assessed here. Furthermore, the morphology and composition of residual ash was found to be strongly influenced by the nanofiller presence. Upon thermal degradation of the NEP, the nanofillers surfaced with the brittle degraded thermoplastic matrix of the residual ash holding them together, thereby making them prone to release under mechanical or weathering conditions. The mass concentration of the nanofillers was significantly enhanced in the residual ash as compared to that in the original NEP.

The findings so far raise important questions and concerns regarding exposure to released engineered

nanomaterials in byproducts to professionals (incineration facility employees, fire-fighters) or consumers (incidental fires in buildings). Disposal of residual ash in landfills raises environmental health and safety (EHS) concerns regarding possible release of ENMs in environmental media as a result of the thermal degradation of the polymer and under weathering conditions. Thus, the generated data and developed methodology are of crucial importance in addressing the life-cycle EHS implications of NEPs and will facilitate the development of safer-by-design NEP approaches, exposure control practices and a risk assessment framework that is based not on "raw" ENM properties, but on real-life exposures and toxicological properties of associated byproducts.

108.13 Case study on risk evaluation of silver nanoparticle exposure from antibacterial sprays containing silver nanoparticles

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With the recent widespread application of nanotechnology to consumer products, consumer exposure to nanomaterials released from these products has also increased. As a result, there is a growing concern about the risks this may have on human health and the environment. Many of the available products containing silver nanoparticles (AgNPs) are household products, along with machinery used in workplaces. While many studies have already investigated the levels of AgNPs contained in consumer products, this study investigates the release of AgNPs from sprays that contain these particles. Using an exposure simulation chamber as the setting for the experiment, various instruments, including a scanning mobility particle sizer (SMPS), condensation particle counter (CPC), dust monitor, and mixed cellulose esters (MCE) filters, are connected to the chamber to measure the exposure levels of AgNPs when using the sprays. When evaluating the risk of inhalation exposure using the margin of exposure (MOE), spraying a whole can and spraying an air conditioner both resulted in a high-risk concern level with a MOE ranging from 59-132 that was much lower than the no-risk concern level of 1000. Plus, the dermal exposure levels with a single layer of clothing were estimated at 2-50 mg/kg. However, when considering the results of another acute dermal toxicity study at concentrations up to 2,000 mg/kg/day and recent 28-day dermal toxicity data up to 1,000 mg/kg, neither of which showed any significant toxicity or systemic absorption in the blood or urine, the current dermal exposure levels were negligible when compared with the MOE no-risk concern level of 1000. Therefore, the current results showed the possibility of high-risk inhalation exposure to AgNPs released when using antibacterial sprays.

108.14 A case study on risk evaluation of printed electronics using nanosilver ink

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With the ever-increasing development of nanotechnology, our society is being surrounded by possible risks related to exposure to manufactured nanomaterials. The consumer market already includes many products that contain silver nanoparticles (AgNPs), including various household products, such as yoga mats, cutting boards, running shirts, and socks. Plus, there is a growing concern over the release of AgNPs in workplaces related to the manufacture and application of nanomaterials. Therefore, this study investigated the release of AgNPs during the operation of a printed electronics printer. Using an exposure simulation chamber, a nanoparticle collector, SMPS (scanning mobility particle sizer), CPC (condensation particle counter), dust monitor, and MCE (mix cellulose esters) filters are all connected to measure the AgNP exposure

levels when operating a printed electronics printer. As a result, a very small amount of AgNPs was released during the operation of the printed electronics printer, plus the number of AgNPs inside the exposure simulation chamber was lower than that outside. Plus, when evaluating the potential risks for consumers and workers using a margin of exposure (MOE) approach and target MOE of 1000, the operational results far exceeded the target MOE in this simulation study and in a previous workplace exposure study. Therefore, the overall results indicate a no-risk concern level in the case of printed electronics using nanosilver ink.

108.15 Evaluation of darkfield microscopy and hyperspectral imaging for analysis of airborne carbon nanotubes captured from occupational settings

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Current best-known methods for engineered nanomaterial (ENM) exposure assessment in occupational environments include the capture of airborne ENMs onto filter media. The standard method for the detection of ENMs captured onto filter media is direct visualization via transmission electron microscopy (TEM) for particle sizing, count, and morphology, coupled with compositional analysis, typically by energy-dispersive spectroscopy (EDS). This method is low-throughput, expensive, and time- and resource-intensive. Enhanced darkfield microscopy (EDFM) with hyperspectral imaging (HSI) analysis is being evaluated as a high-throughput screening technique to rapidly identify filter media samples that contain ENMs of interest that may then move on for further, more intensive TEM/EDS analysis. Building upon a preliminary study lead by NIOSH, we are further exploring the use of EDFM/HSI for the rapid visualization and identification of carbon nanotubes (CNTs) captured on mixed cellulose ester (MCE) filter media. We will compare the protocol we develop for EDFM/HSI of CNTs on MCE filter media to conventional TEM methods for accuracy, reliability, and precision of this new screening method. Future directions include expanding the EDFM/HSI protocol to other ENMs and to polycarbonate (PC) filter media samples.

108.16 Information resources for exposure assessment of engineered nanomaterials

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Nanoinformatics is the science and practice of determining which information is relevant to meeting the objectives of the nanoscale science and engineering community; and then developing and implementing effective mechanisms for collecting, validating, storing, sharing, analyzing, modeling, and applying that information; and then confirming that appropriate decisions were made and that desired mission outcomes were achieved as a result of that information; and finally conveying experience to the broader community, contributing to generalized knowledge, and updating standards and training. In our roles as information customers, creators, curators, and analysts, this definition should guide our collaborations to effectively assess and manage exposures to engineered nanomaterials. Key questions include: Is a hazard present? Is there exposure to that hazard? What is the resulting risk? How can that risk be managed? and Is the risk management approach achieving the desired protection?

The development of information resources such as the Nanomaterial Registry (nanomaterialregistry.org) has required our community to identify nanomaterial characteristics that are both meaningful and measurable and to validate reproducible protocols and practices for collecting information about those characteristics. The identification of key nanomaterial characteristics for exposure assessment is benefiting from a combination of field measurements (e.g., cdc.gov/niosh/topics/nanotech/) to determine what is actually present across the nanomaterial life-cycle, as well as laboratory investigations of how materials with those characteristics behave under

environmentally, biologically, or industrially relevant conditions.

Collaborations such as the National Nanotechnology Initiative signature initiative on Nanotechnology Knowledge Infrastructure—Enabling National Leadership in Sustainable Design (nano.gov/signatureinitiatives) are developing unifying concepts such as data-readiness levels and approaches for sharing and ensuring the reproducibility of data and experimental results. Community-based resources such as the GoodNanoGuide (nanohub.org/groups/gng) are helping to share information in a manner that is relevant, reliable, and actionable. New generations of sensors will undoubtedly be needed to characterize nanomaterials efficiently and affordably and collaborations on that front are available through the signature initiative on Nanotechnology for Sensors and Sensors for Nanotechnology: Improving and Protecting Health, Safety, and the Environment (nano.gov/signatureinitiatives).

The extensive list of links to information on the environmental health and toxicology of nanotechnology and human health at sis.nlm.nih.gov/enviro/nanotechnology.html illustrates both our current resources and our opportunities to improve our identification, creation, curation, analysis, and meaningful application of exposure assessment information in support of safe nanomaterial applications.

(The findings and conclusions in this abstract are those of the author and do not necessarily represent those of the National Institute for Occupational Safety and Health.)

108.17 Nanotechnology Knowledge Infrastructure (NKI): Enabling national leadership in sustainable design — Nanotechnology Signature Initiative

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The knowledge infrastructure has been identified by the Federal agencies participating in the National Nanotechnology Initiative as a focus area that may be more rapidly advanced through enhanced coordination and collaboration as a Nanotechnology Signature Initiative (NSI). The goal of the Nanotechnology Knowledge Infrastructure (NKI) Signature Initiative is to provide a community-based, solutions-oriented knowledge infrastructure to accelerate nanotechnology discovery and innovation. The NKI has four thrust areas that focus efforts on cooperative interdependent development of: (1) a diverse collaborative community; (2) an agile modeling network for multidisciplinary intellectual collaboration that effectively couples experimental basic research, modeling, and applications development; (3) a sustainable cyber-toolbox to enable effective application of models and knowledge to the design of nanomaterials; and (4) a robust digital nanotechnology data and information infrastructure to support effective data sharing, collaboration, and innovation across disciplines and applications. Agencies involved include Consumer Product Safety Commission, Department of Commerce (National Institute of Standards and Technology), Department of Defense, Department of Health and Human Services (Food and Drug Administration, National Institutes of Health, National Institute for Occupational Safety and Health), Department of Labor (Occupational Safety and Health Administration), Environmental Protection Agency, National Aeronautics and Space Administration, and National Science Foundation.

108.18 Nanotechnology for sensors and sensors for nanotechnology: Improving and protecting health, safety, and the environment — Nanotechnology Signature Initiative

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Sensors have been identified by the Federal agencies participating in the National Nanotechnology Initiative as a focus area that may be more rapidly advanced through enhanced coordination and collaboration as a Nanotechnology Signature Initiative (NSI). The goals of this NSI are to support research on nanomaterial properties and development of supporting technologies that enable next-generation sensing of biological, chemical, and nanoscale materials. This interagency effort coordinates and stimulates creation of the knowledge, tools, and methods necessary to develop

and test nanosensors and to track the fate of nanomaterials. The current thrust areas for this NSI are to: (1) develop and promote adoption of new technologies that employ nanoscale materials and features to overcome technical barriers associated with conventional sensors; and (2) develop methods and devices to detect and identify nanomaterials across their lifecycles. Agencies involved include Consumer Product Safety Commission, Department of Commerce (National Institute of Standards and Technology), Department of Defense, Department of Health and Human Services (Food and Drug Administration, National Institutes of Health, National Institute for Occupational Safety and Health), Environmental Protection Agency, National Aeronautics and Space Administration, National Science Foundation and the U.S. Department of Agriculture (National Institute of Food and Agriculture).

108.19 Revisiting the safety of food-grade nanomaterials: Towards more realistic and relevant studies

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Food-grade engineered nanomaterials are being used in large quantities in various food products (FNM). Although they are generally assumed to be safe, nanotoxicology on this class of nanomaterials is limited and the topic is generally understudied. Some major limitations of existing studies related to FNM nanotoxicity include: (i) use of surrogate non-food grade nanomaterials for testing; (ii) inadequate characterization of materials in dry powder form and in the test media; (iii) limited data on ENM biokinetics and dissolution in biological fluids (*in vitro* and *in vivo*); (iv) lack of standardized dispersion protocols and *in vitro* dosimetry considerations; (v) limited consideration on the use of realistic doses for both *in vitro* and *in vivo* studies, including *in vitro* to *in vivo* dose equivalencies.

The objective of the current study is to better understand the safety of food-grade ENM by systematically documenting and addressing some of the aforementioned limitations. A panel of 11 model FNMs, including – titania, silica, iron oxide and zinc oxide, were acquired from the respective manufacturers. Extensive physicochemical and morphological characterization of these materials in dry powder and cell culture media was accomplished using multiple complementary techniques (SF-ICP-MS, TEM, XRD, XPS, FTIR, BET, etc.). Furthermore, the most recent standardized dispersion and dosimetry protocols developed at Harvard (VCM-ISDD) were used to estimate in vitro dosimetry over time in relevant cell cultures representative of the digestive system (C2BBe1-clone of Caco-2 and, HOK-human oral keratinocytes) in preparation for ongoing *in vitro* and *in vivo* nanotoxicity work. The poster will present data on the PCM characterization of these FNM and in vitro dosimetry, including implications of these findings on the current understanding of *in vitro* and *in vivo* nanotoxicity and regulation of their use in food.

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