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Nanoscale zero-valent iron impregnation of covalent organic polymer grafted activated carbon for water treatment

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Abstract Program



Nanoparticle Analysis and Surface Chemistry

Oral Presentations



Monday, August 15, 2016
Nanoparticle Analysis and Surface Chemistry I
3:50 PM

Characterisation challenges for nanoparticles in complex matrices

Åsa Jämting, National Measurement Institute Australia
Jessica Butcher, Yong Yeow Tang, Kirsty Evans, Victoria A. Coleman, and Jan Herrmann

The number of consumer products that incorporate engineered nanomaterials has grown significantly over the past decade. The prevalent use of engineered nanoparticles (NPs) in a wide and ever-broadening range of market sectors, including personal-care products, food and architectural coatings, has contributed to the increased need for detection, characterisation and quantification of nanomaterials in complex matrices to support not only their development but also the assessment of their environmental impact as well as their regulation and responsible use. Recent studies report on the detection of NMs in complex matrices such as environmental media and foods, however, quantification of NPs still remains a challenge. A promising approach for characterisation of NPs in complex matrices combines a separation step to fractionate particulate material with a number of different characterisation detectors that provide information about properties such as size, molecular weight, number concentration and chemical composition.

Sensitivity, resolving power for multi-modal particle size distributions (PSDs) and influence of the suspension matrix are important variables to explore as the need for quantitative characterisation methods for complex NP-containing samples increases. Here, we compare and contrast several particle sizing techniques including separation techniques such as sedimentation field flow fractionation and differential centrifugal sedimentation with dynamic light scattering, laser diffraction, particle tracking analysis and transmission electron microscopy, using two different classes of samples.

Firstly, carefully designed multi-modal suspensions of citrate-stabilised gold nanoparticles with narrow PSDs were used to evaluate instrument sensitivity and resolving power for particle sizing. Secondly, to assess the ability to accurately measure samples in more complex matrices, samples containing titanium dioxide NP suspensions with broad PSDs in the nano and non-nano range were also studied, in matrices such as ultrapure water, ultrapure water with surfactant addition, and sucrose solutions with increasing amount of sugar content. The results of this study highlight the strengths and weaknesses of the different measurement techniques used to characterise particles with both monomodal and more challenging multi-modal PSDs suspended in matrices of varying complexity, and demonstrate the value in using multiple complementary techniques to address measurement challenges.

Monday, August 15, 2016
Nanoparticle Analysis and Surface Chemistry I
4:10 PM

Investigating aggregate morphology of planar engineered nanomaterials

S. Drew Story, University of California, Riverside

A systematic investigation was performed to confirm the viability of a static light scattering (SLS) technique to characterize aggregate morphology of two-dimensional engineered nanomaterials (2-D ENMs). Aggregation of graphene oxide (GO) and lithiated-molybdenum disulfide (Li-MoS₂) was studied and compared to that of a spherical reference colloid, carboxylate-modified latex nanoparticles. The critical coagulation concentration (CCC) for all dispersions was determined by an analysis of aggregation kinetics using dynamic light scattering, and this elucidated the transition from the reaction-limited aggregation (RLA) regime to diffusion-limited aggregation (DLA). The findings of this study supported the trend predicted by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of an increase in attachment efficiency as the 2-D ENM colloids destabilize. For all nanomaterials, as ionic strength approached the CCC, fractal dimension decreased; whereas, any increase in ionic strength beyond the CCC did not yield significant change in fractal dimension. Across comparable primary particle sizes, and using both carbonaceous (GO) and inorganic (Li-MoS₂) 2-D ENMs, this study supports the use of SLS for the measurement of fractal dimension for two-dimensional materials. An additional examination of aggregate morphology in both RLA and DLA regimes is being conducted via cryogenic transmission electron microscopy (cryo-TEM). In this technique, colloidal suspensions are flash frozen before being imaged in their then current aggregation state. This additional characterization may further support the hypothesis that SLS is an acceptable technique to determine fractal dimension of 2-D ENMs.

Monday, August 15, 2016
Nanoparticle Analysis and Surface Chemistry I
4:30 PM

Utility of gold-labeled core/shell nanoparticles as a tool for examining the environmental fate, transport, and toxicity of titanium dioxide nanomaterials

Alyssa Deline, Oregon State University
William Young, Jeffrey A. Nason

Titanium dioxide nanoparticles (TiO₂ NPs) are produced for numerous industrial and commercial applications, many of which will lead to the direct release of these materials into natural waters and wastewater streams with a relatively high abundance of naturally occurring titanium. It is critical that engineered TiO₂ NPs are able to be detected and quantified in complex systems containing background titanium. This is often achieved through the use of techniques like the isotopic or fluorescence labeling of TiO₂ NPs, but researchers require a labeling method that can be accurately quantified using accessible techniques, while maintaining the relevant physicochemical properties of unlabeled particles. To that end, gold-labeled, core/shell TiO₂ NPs (Au@TiO₂ NPs) were developed as a traceable material sensitive to multiple instrumental methods. Gold core particles were synthesized using a seeded-growth procedure and coated by hydrolyzing titanium isopropoxide on the gold surfaces. The core/shell structure of the Au@TiO₂ NPs was confirmed using electron microscopy. The properties of the Au@TiO₂ NPs relevant to environmental behavior were compared to that of unlabeled TiO₂ particles, with the goal of modifying the synthetic procedures to minimize differences. The labeled NPs have been accurately quantified down to 1.5 ppb Ti in an aqueous solution containing background titanium, using the known gold-to-titanium ratio of the core/shell particles. Ongoing experiments include spike-and-recovery demonstrations in natural waters, as well as a toxicity assay containing multiple trophic levels of organisms. Preliminary results will be discussed.

Monday, August 15, 2016
Nanoparticle Analysis and Surface Chemistry I
4:50 PM

Photochemical transformations of polyvinylpyrrolidone coatings on gold nanoparticles

Stacey Louie, National Institute of Standards and Technology (NIST), Materials Measurement Science Division (MMSD)

Justin M. Gorham, NIST - MMSD; Vincent A. Hackley, NIST - MMSD; Current affiliation for S.M. Louie - University of Houston, Dept of Civil and Environmental Engineering, Houston, TX 77004

Transformations of adsorbed polymeric coatings can significantly change the environmental fate and toxicity of engineered nanoparticles (NPs), but these transformations have not yet been fully explored. In this study, we investigate the photochemical transformations of a commonly used polyvinylpyrrolidone (PVP) coating on gold nanoparticles under controlled ultraviolet irradiation. The physical and chemical properties of the PVP-coated NPs were evaluated using a suite of methods, including dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), and attenuated total reflectance \hat{a} Fourier transform infrared (ATR-FTIR) spectroscopy. Photochemical oxidation of the coating was observed by both XPS and ATR-FTIR analyses. While the XPS analysis indicated only minimal change in the C: Au elemental ratio, DLS measurements showed a significant decrease in the hydrodynamic diameter of the coated NPs within 24 h of UV irradiation, suggesting a conformational change of the coating may have occurred upon oxidation. These transformations resulted in partially diminished colloidal stability of the NPs. Implications of the physicochemical coating transformations for the surface interactions of the NPs will also be discussed.

Tuesday, August 16, 2016
Nanoparticle Analysis and Surface Chemistry II
9:30 AM

Optimized strategies for the characterization of titanium dioxide-nanoparticles in complex environmental samples using centrifugal-FFF hyphenated to ICP MS/MS

Florian Dutschke, Helmholtz-Zentrum Geesthacht
Daniel Proefroc, Helmholtz-Zentrum Geesthacht; Johanna Irrgeher, Helmholtz-Zentrum Geesthacht

During the last decades nanoparticles (NP), in particular TiO₂-NP, have been increasingly used as additives in products of daily use (ZÄnker and Schierz 2012, Gao et. al. 2013) like sunscreens, toothpaste, paints as well as products for medical and environmental use. As a consequence of the significantly increased production volume of TiO₂-NP an increasing amount of these particles is constantly released into the environment.

Initially, TiO₂-NP were considered as inert and non-toxic, neither for the environment, nor for humans. Recent studies (e.g. by Jacobasch et. al. (2014), Zhu et. al (2014) and Soto et. al (2013)) showed toxic effects related to the presence of TiO₂-NP on different marine organisms and humans. Due to this fact concern arises about their presence and potential adverse effects on the environment in terms of a good chemical status.

The quantity and the chemical and physical state of the released nanoparticles in the environment have not been studied sufficiently. Their low concentration, the wide size-distribution as well as matrix related effects like agglomeration, resuspension as well as spectroscopic interferences are challenging for the analysis of TiO₂-NP by techniques such as field-flow-fractionation (FFF) and inductively coupled plasma mass spectrometry (ICP-MS). Thus new and/or optimized analytical strategies are required.

Here a method for the detection and separation of TiO₂-NP using centrifugal-field-flow-fractionation hyphenated to ICP-MS/MS is presented, showing recovery rates of up to 90 % and detection limits down to 0.02 mg kg⁻¹ based on the analysis of NIST SRM 1898. Additionally, different industrially used TiO₂-NP were characterized for their elemental pattern and particle size-distribution in solution.

Further, a method for extraction and enrichment of nanoparticles from natural sediment samples as well as water samples is presented, revealing a recovery rate of up to 90 % and a reduced standard error deviation of 5 % for the extraction. Finally, the results are compared with the characteristics of industrially used TiO₂ particles.

Tuesday, August 16, 2016
Nanoparticle Analysis and Surface Chemistry II
9:50 AM

Dissolution behavior of Silver Nanoparticles and Formation of Secondary Silver Nanoparticles in Municipal Wastewater by Single Particle ICP-MS

Mehrnoosh Azodi, McGill University
Subhasis Ghoshal

The anticipated increases in the use and the resulting releases to the environment of Ag nanoparticles (NPs) necessitates a better understanding of the environmental transformation of Ag NPs to effectively manage environmental risks. Dissolution of Ag NPs is an important environmental transformation process because it releases dissolved Ag into the aquatic environment and alters the size of Ag NPs, both of which can influence the toxicity characteristics of NPs. A significant fraction of Ag NPs used in various products are expected to be released with wastewater (WW) but the factors controlling the dissolution of Ag NPs and the fate of Ag⁺ ions released in a complex matrix such as WW are currently poorly understood. In this study, dissolution of 80 nm Ag NPs in the municipal WW samples collected from a municipal WW treatment plant near Montreal, QC, were studied, with two common particle coatings (citrate and PVP) and at two particle concentrations, 10 and 1000 ppb. 10 ppb is in the range of concentrations expected in WW and 1000 ppb represents concentrations commonly used in recent dissolution studies of Ag NPs. Our investigations determined that wastewater organic and inorganic constituents, as well as NP concentrations influenced the rates of dissolution, and dissolved Ag reformed into small (~20 nm) NPs over time. Single particle inductively coupled plasma mass spectrometry (SP ICP-MS) was used to determine the mean size and particle size distribution of the NPs and the dissolved silver concentrations to quantify the rate and extent of dissolution of Ag NPs. The WW matrix was inhibitory to the dissolution and the Ag NPs dissolved considerably less (~47%) in WW effluent as compared to DI water. In addition, the Ag NPs dissolved substantially more mass per particle at lower particle concentration of 10 ppb (5- 106 particles/mL) than at 1000 ppb (5- 108 particles/mL) ppb. As a result, the Ag NPs at 10 ppb reached 43.5 ± 0.5 nm whereas it only decreased to 63.1 ± 0.74 nm after 168 h exposure to WW effluent. Time-of-Flight Secondary Ion Mass Spectrometry (TOF ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analyses suggested close association of WW dissolved organic carbon (DOC) as well as sulfides (organic and inorganic) on the surface of the Ag NPs, both of which likely contributed to the decrease in dissolution extent and rate. The released Ag⁺ was not stable in the dissolved phase and TEM analyses confirmed the re-formation of secondary Ag NPs from the dissolved Ag⁺ in WW.

Tuesday, August 16, 2016
Nanoparticle Analysis and Surface Chemistry II
10:10 AM

Multi-element single-particle fingerprints for the detection of engineered cerium oxide nanoparticles in soils

Antonia Praetorius, University of Vienna

Frank von der Kammer (University of Vienna)*-giving talk, Alexander Gundlach-Graham (ETH Zurich), Eli Goldberg (ETH Zurich), Jana Navratilova (University of Vienna), Andreas Gondikas (University of Vienna), Detlef Guenther (ETH Zurich), Thilo Hofmann (University of Vienna)

The lack of analytical methods to detect and quantify engineered nanomaterials (ENMs) in complex natural matrices (e.g. soils and sediments) remains one of the major challenges in the fate and risk assessment of these materials. Conventional techniques are often not able to differentiate engineered nanoparticles (ENPs) from a high background of natural counterparts. For example, in the case of engineered cerium oxide nanoparticles (CeO₂ ENPs), detection is hindered by the presence of natural Ce-containing minerals of similar size and concentration ranges. A promising strategy to identify CeO₂ ENPs against the often high natural background levels is to take advantage of the different element ratios of natural versus engineered Ce-containing NPs. The Ce to La ratio has been found to be relatively stable at about 2:1 in natural environments, while CeO₂ ENPs show a Ce:La ratio of more than 1000:1. To detect CeO₂ ENPs in soils and sediments, a method to assess the elemental ratios on an individual particle level is required.

Here we present a new approach using a conventional inductively coupled plasma source (ICP) coupled with a time-of-flight (TOF) mass spectrometer. This new ICP-TOFMS instrument enables the simultaneous measurement of multiple elements at high sensitivity and $\hat{\text{A}}\mu\text{s}$ time resolution. It provides element fingerprints on an individual particle level. We demonstrate the applicability of this method for the detection of CeO₂ ENPs in complex matrices on a case study using natural soils spiked with different concentrations of CeO₂ ENPs far below the natural background. Our results show that we can differentiate Ce-only containing ENPs from Ce- and La-containing natural particles using the ICP-TOFMS in single-particle mode. A machine-learning based data processing method is employed to identify and take full advantage of the unique multi-element fingerprints of both the engineered and natural the Ce-containing particles. We are thereby able to detect CeO₂ ENPs in real soils at environmentally relevant concentrations in the ppb range. This new method represents an important advancement for the detection of ENPs in natural samples and can likely be applied to a wide range of other ENPs in the future.

Tuesday, August 16, 2016
Nanoparticle Analysis and Surface Chemistry II
10:30 AM

Evaluation of titanium dioxide nanoparticle heteroaggregation with suspended particulate and natural organic matter analogues

Danielle Slomberg, CEREGE

Labille, J. (CEREGE); Pariat, A. (CEREGE); Praetorius, A. (University of Vienna); Ollivier, P. (BRGM); Radakovitch, O. (CEREGE); Sani-Kast, N. (ETH Zurich); Scheringer, M. (ETH Zurich & RECETOX)

The fate of engineered nanoparticles (ENPs) in natural aqueous environments is influenced by ENP dispersion/transport and aggregation/deposition related to environmental factors as well as those intrinsic to the nanoparticles themselves. For example, at environmentally relevant concentrations ($\hat{1}$ _g/L), TiO₂ ENPs likely have a higher probability of interacting with suspended particulate matter (SPM) and natural organic matter (NOM) present at mg/L or greater concentrations in natural surface waters, rather than with themselves. With both high specific surface area and reactivity, the SPM and NOM may act as TiO₂ ENP carriers in the water column, strongly affecting their fate and transport via the heteroaggregation process. Herein, previously identified and characterized SPM and NOM compositions of the Rhone River [1,2], a major European river, were used to guide the selection of relevant analogues for mechanistic evaluation of TiO₂ ENP fate in surface waters. The TiO₂ ENPs ($\hat{1}$ _g/L) were first spiked into synthetic riverine waters containing one of the main SPM analogues (e.g., quartz, calcite, chlorite, feldspar, muscovite). With rapid heteroaggregation and subsequent sedimentation, the TiO₂ ENPs demonstrated a significant affinity for several of the SPM analogues, especially quartz and calcite. In addition to determining the ENP/SPM heteroaggregation kinetics and attachment efficiencies, the influence of NOM on the TiO₂ ENP fate and behavior was also assessed. Four common families of NOM analogues (i.e., proteins, polyhydroxy aromatics, polysaccharides, and amino sugars) were added to the SPM-containing synthetic waters to evaluate the role of NOM on the TiO₂ ENP compartmentalization. Together, these mechanistic data, coupled to a river-scale fate model, will aid in ranking potential TiO₂ ENP fate scenarios and assessing their risk within natural aqueous environments. This work was funded by the French National Research Agency and the Swiss FOEN as NANOHETER under the frame of SIINN.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
9:30 AM

Analysis of nanosilver in a lake ecosystem using fast, continuous data acquisition capabilities of the Nu Attom HR ICP-MS

Karla Newman, Trent University
Chris Metcalfe, Trent University; Jonathan Martin, Trent University; Phil Shaw, Nu Instruments; Ariane Donard, Nu Instruments

Single particle ICP-MS (spICP-MS) is proving to be a useful tool for the characterization and quantification of metallic nanoparticles in suspension. However, dwell times in the millisecond range and an imposed settle time between signal integrations are not conducive to the measurement of the short (300 - 400 us) transient signals generated by single particle events. Therefore, a number of studies have focused on fast, continuous data acquisition that minimises measurement bias due to the recording of partial events, or multiple events occurring within a single integration period. The discrimination of single particle events from the signal background is also intrinsically dependent on the dwell time, and as such determines the minimum detectable particle size. The work presented will describe a new spICP-MS analytical capability available on the Nu AttoM HR-ICP-MS, whereby data acquisition is possible with dwell times down to 10- μ s. We will describe the unique detection system of the AttoM, which does not use the slow analogue stages of the detector at high (> 5 M cps) count rates, and allows dynamic range extension with sub-millisecond dwell times. Determining how nanoparticle sizes and concentrations evolve over time in natural ecosystems is a challenge using conventional spICP-MS methods, in part due to the relatively small particle sizes (< 30 nm) that can result from particle dissolution over time. In this work, we characterised and quantified silver nanoparticles (AgNPs) of different sizes prepared from commercially available suspensions (i.e. NanoComposix) and also analysed AgNPs in natural waters. We observed improvements in size detection limits to <20 nm using the new, fast, continuous data acquisition capabilities of the Nu Attom HR ICP-MS. Samples of water were collected from a lake dosed with AgNPs (nominal size range 50 nm; PVP capped), as part of the Lake Ecosystem Nanosilver (LENS) project. This study, carried out in Lake 222 in the Experimental Lakes Area in north-western Ontario, Canada was conducted to investigate the fate and effects of AgNPs on aquatic ecosystems. The analytical results generated by the Nu Attom HR ICP-MS showed that the size range of the AgNPs suspended in the water column of Lake 222 was consistent with the size of the AgNPs in the stock suspension added to the lake, with little evidence of agglomeration, and the concentrations of dissolved Ag in the water column were low (i.e. <1 ppb).

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
9:50 AM

Tracing multi-isotopically labelled CdSe/ZnS quantum dots in the environment: an assessment of the method's strengths and limits

Nurul Izyan Supiandi, Institut de Physique du Globe de Paris (IPGP)
N. Izyan Supiandi, Y. Sivry, G. Charron, M. Tharaud, J.-M. Guigner, and M. F. Benedetti

Manufactured nanoparticles (NPs) are highly susceptible to being released in the environment. However, studies on their fate and behavior presented in the literature are often carried out at concentrations far from those in real environmental media [1], because of the difficulty to detect NPs in complex and "noisy" matrices. Nevertheless, changes in NPs concentration are known to affect its physicochemical behavior. In order to overcome analytical barriers while working at representative realistic concentration, innovative tools such as HR-ICP-MS and non-traditional stable isotopes (isotopically modified NPs [2] or "spiked") have been used. 7 nm sized isotopically labelled quantum dots (QDs), CdSe/ZnS core-shell structure were synthesized, enriched in ^{68}Zn , ^{77}Se and ^{111}Cd . These multi-spiked QDs were disseminated at very low concentrations (from 0.1 ng/L to 5 $\mu\text{g/L}$) in aquatic media, and the isotopic compositions were determined by HR-ICP-MS. On this basis, the initial QDs concentrations were calculated [3], in order to assess the Lowest Quantifiable QDs Concentration (LQC) according to the medium and to the element isotopically labelled. Our results allow to assess the detection and quantification limits of spiked QDs in complex matrices such as river water, seawater and estuarine system. The feasibility of isotopic labeling at very low concentrations has been demonstrated: spiked Zn, Cd and Se issued from QDs were quantifiable at 1, 0.3 and 20 ng/L respectively in a media (HNO_3 2%) not already containing the same natural elements. In contrast, these limits hardly reach 50 and 30 ng/L for spiked Zn and Cd respectively in seawater, and 50 and 0.3 ng/L respectively in Seine river water. The results obtained in this experimental work are applicable for studying QDs fate and behavior in most aquatic media.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
10:10 AM

Greater biouptake and aquatic to terrestrial transfer in wetlands exposed to chronic AgNP addition compared to a one time pulse

Benjamin Colman, University of Montana
Leanne F. Baker, University of Waterloo; Cole W. Matson, Baylor University;
Ryan S. King, Baylor University; Emily S. Bernhardt, Duke University

While the majority of ecotoxicological studies of engineered nanomaterials focus on short-duration exposures of high concentrations of freshly-synthesized nanomaterials, exposures in natural systems are likely to be characterized by being long-term, low-concentration, and chronic additions of transformed nanomaterials. How might these two divergent exposure scenarios drive the uptake and impacts of engineered nanomaterials? To address this question, we conducted a yearlong wetland mesocosm experiment with mesocosms exposed to an identical total amount of silver as either: a one-time pulse of zerovalent silver nanoparticles (AgNPs; Pulse-Ag(0) treatment); 52 weekly additions of zerovalent AgNPs (Chronic-Ag(0) treatment); and 52 weekly additions of sulfidized AgNPs (Chronic-Ag₂S treatment). We then measured silver concentration three times weekly, measured silver concentrations in three core species of aquatic organisms quarterly, and measured complete distribution of silver in sediment, water, and across all organisms at 30 days and 365 days. We found that concentrations in the water column and in most organisms were similar between Chronic-Ag(0) and Pulse-Ag(0) treatments by 30 days, with the Chronic-Ag(0) treatment being up to an order of magnitude higher in some taxa at 365 days into the experiment. Patterns in the Chronic-Ag₂S treatment were similar in timing and magnitude to the Chronic Ag(0) treatment, suggesting that even the relatively insoluble and less toxic Ag₂S-NPs are still moving through the ecosystem and accumulating in organisms. We also saw evidence at both 30 days and 365 days of trophic transfer from the aquatic compartment to a terrestrial predator, suggesting the possibility of reciprocal subsidies of nanoparticle contaminants between aquatic and terrestrial ecosystems.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
10:30 AM

Biofilm formation and biodegradation of carbon nanotube-polymer nanocomposites

Howard Fairbrother, Johns Hopkins University
Goodwin, D.G.; Phan, D.C.; Xia, Z.; Boyer, I.B.; Devahif, T.; Gordon, T.B.;
Kuwama, L.; Lu, X.; Gao, C.; and Bower, E.J.

Carbon nanotube/polymer nanocomposites (CNT/PNCs) are being increasingly produced for consumer applications as a result of the enhanced materials properties imparted to the polymer by CNT incorporation; these properties can include increased mechanical strength and electrical conductivity. However, upon disposal, CNT/PNCs can lead to adverse effects in the environment due to CNT release, CNT/PNC persistence, and CNT/PNC transformation pathways that expose CNT fillers. In particular, microbial populations can interact and potentially transform CNT/PNCs via biodegradation in landfills, surface waters, and wastewater treatment plants. In this study, the impact of CNTs on biofilm formation and biodegradation of CNT/PNCs was assessed under accelerated conditions using biodegradable polymer matrices. Under single culture conditions, cell death of *Pseudomonas aeruginosa* was observed when in direct contact with CNTs at the surface of a CNT/PNC. However, viable biofilm formation continued above the dead layer of cells as indicated by LIVE/DEAD staining. The effect of this dead layer on the biodegradation of the underlying polymer matrix was then evaluated using mass loss studies and SEM characterization. The results indicate that the presence of CNTs can retard biodegradation and that CNT/PNCs above a certain CNT loading threshold (> 2% w/w) can become persistent. In contrast, biodegradation of CNT/PNCs under mixed culture conditions led to complete polymer matrix degradation and generated a brittle, CNT mat. CNT release as a result of biodegradation was also measured using single-particle ICP-MS, with residual metals used as a proxy for CNT release. Potential benefits and implications of CNT/PNC persistence, degradation, and release will be discussed.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
11:20 AM

Detection and quantification of engineered nanoparticles in biosolids from wastewater treatment plants(WWTP)

Arshath Abdul Rahim, McGill University
Subhasis Ghoshal

Engineered nanoparticles (ENPs) are being extensively used in a variety of industrial and consumer products due to their properties leading to an increased release in the environment. A significant fraction of ENPs entering WWTP is likely to be removed with settled sludge. Currently, there is a scarcity of data on the presence and abundance of ENPs in municipal sludge and biosolids, and robust data is needed for conduction environmental risk assessments and biouptake assessments for the ENPs. Biosolids are being increasingly applied on agricultural lands as natural fertilizers. The study involves the development and optimization of methods to detect the sizes and concentrations of several common metal ENPs in biosolids by various extraction procedures involving sequential dilution, sonication and proteinase enzyme biomass digestion. Aqueous extracts were then analyzed by Inductively- Coupled Plasma Mass Spectrometry in single particle mode (SP ICP-MS). The analysis was optimized and validated by performing control experiments with biosolids aqueous extracts spiked with ENPs of specific sizes. Development of this method enabled the detection of metallic ENPs in aqueous extracts of biosolids with approximate mean sizes ranging from 20 to 150 nm for Cu, Ag and Zn with concentration in the range of 10^7 to 10^9 NPs/g of dry biosolids in samples from eight different WWTP across Canada. The presence of different ENPs in the biosolids samples was also confirmed with transmission electron microscopy. The water extractable ENP concentrations are likely a small fraction of the total ENP concentrations in the biosolids as the and recovery of spiked ENPs in biosolids was found to be decrease from 93% after contact time of one day to 11% at 30 days The estimation of ENP size and water-extractable concentrations in biosolids can provide us with important data for environmental risk assessments and also advances analytical capabilities for the study of environmental fate and transformation of ENPs in complex environmental matrices.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
11:40 AM

Adsorption of III/V ions to chemical mechanical polishing (CMP) nanoparticles

Xiangyu Bi, Arizona State University
Paul Westerhoff, Arizona State University

The semiconductor industry uses thousands of tons per year of chemical and mechanical planarization (CMP) NPs, yet little is known on their fate and transformation in wastewater systems. In the wastewater after a CMP tool, CMP NPs interact with ions that are derived from the substrate materials, a growing group of which is III/V materials (e.g., InP, GaAs). The environmental health and safety (EHS) of both CMP NPs and III/V ions is highly concerned due to a considerable unknown risk of them. Scarce studies examine the adsorption of III/V ions to the CMPs and the consequential environmental implications.

Thursday, August 18, 2016
Nanoparticle Analysis and Surface Chemistry III
12:00 PM

Physicochemical behaviour of TiO₂ particles in simulated digestive fluids.

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France

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Titanium dioxide is a white metal oxide employed as a pigment, which is commonly used in coatings of candies and chewing-gum. Food-grade TiO₂, referred to as E171 in Europe and INS171 in North America, includes a nano-sized fraction, representing less than 44% of the particles. Due to concerns about TiO₂ nanoparticles (NPs) as potentially hazardous, and in particular after ingestion, the fate of particles in the gastro-intestinal tract is under investigation. In this study, the behavior of food grade TiO₂ and TiO₂ NPs (P25, 25nm) were determined through a standardized static in vitro digestion protocol and compared to the control digestion (with and without the digestion enzymes). After each step of digestion (i.e. saliva, gastric and intestinal step), the size of the particles and the surface charge changes were characterized using laser particle size distribution analysis and zeta potential measurements. Finally, the nature of the adsorbed proteins was determined by denaturing gradient gel electrophoresis (DGGE) after separation from the TiO₂ particles. Our results showed that the agglomeration states and surface charge were found to be dependent on the medium composition. Both food grade and P25 particles agglomerate more strongly in the digestive fluids due to the presence of salts and proteins. Moreover, all TiO₂ samples formed the largest agglomerates once in the intestinal fluid, up to 593 μm for food grade, and 77 μm for P25 particles. DGGE analysis showed that food grade and P25 could interact with different enzymes during the simulated digestion. All TiO₂ samples interacted with the alpha amylase, and even with pepsin for the second batch of one of them. Food grade and nano-TiO₂ do not appear to exist as nanometric entity all along the steps of the in vitro digestion protocol, which is good news considering the concerns about the effects of ingested nano-products. However, these large agglomerates could still be transformed in contact with the epithelium and the adsorption of enzymes could have a major impact on the digestion process, if this interaction was responsible for the inactivation of the enzyme.

Nanoparticle Analysis and Surface Chemistry

Posters



Monday, August 15, 2016
Poster Session I
A-101

Nitrogen vacancies in nanodiamond for background-free imaging and sensing

Margaret Robinson, University of Wisconsin-Madison
Arielle C. Mensch, Eric Melby, Yongqian (Kelly) Zhang, Marco D. Torelli, Dehong Hu, Galya Orr, Joel A. Pedersen, Robert, J. Hamers; Pacific Northwest National Laboratory

The unique optical properties of nitrogen vacancies (NV-) in nanodiamond offer an opportunity to perform background-free imaging in complex environments at the single-particle level. The intensity of fluorescence from NV- centers can be modulated by the application of a microwave field. In complex, heterogeneous systems this ability to selectively modulate the intensity of NV- centers using microwaves can be used to discriminate between fluorescence due to nanodiamonds and fluorescence arising from other sources. Here, we describe experiments aimed at understanding the factors that control the ability to read out NV- center fluorescence and reject background fluorescence. We have characterized the optical response of NV- centers in diamond nanoparticles having different diameters and bearing different numbers of NV- centers using photoluminescence, fluorescence lifetime, and single-particle microscopy. Results of Nv-center modulation via applied microwave fields will be described in the context of background subtraction for imaging and sensing local charges.

Monday, August 15, 2016
Poster Session I
A-102

Investigating Nanoparticle Interactions with Supported Lipid Bilayers using Atomic Force Microscopy

Arielle Mensch, University of Wisconsin Madison
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The growing use of nanotechnology has led to an increased release of nanomaterials into the environment that may come into contact with living organisms. The first point of contact between a nanomaterial and an organism occurs at the cellular membrane. The ability to model the cellular membrane in the laboratory and characterize the interactions with nanoparticles can provide insights into understanding these interactions. We utilize the vesicle fusion method to construct supported lipid bilayers, a mimic for the cellular membrane, composed of various biomolecules, such as phospholipids, cholesterol, and sphingomyelin. Due to the low concentration of the released nanoparticles and the inherent need for in situ characterization methods to model environmentally relevant situations, novel analytical approaches, as well as combinations of approaches, are necessary to probe the nano-bio interface. We have characterized our model membrane systems with atomic force microscopy (AFM) and fluorescence microscopy. Efforts for correlating the two techniques are currently being pursued and will be discussed. Furthermore, we use AFM to study the interaction between positively charged diamond nanoparticles and supported lipid bilayers to corroborate quartz crystal microbalance with dissipation results. Our results show that less attachment of positively charged nanodiamond is observed to more negatively charged phospholipid bilayers, suggesting chemical driving forces beyond electrostatics are involved in these interactions.

Monday, August 15, 2016
Poster Session I
A-103

Developing Single Particle ICP-MS analysis for the detection of complex nanoparticles

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Single Particle ICP-MS (SP-ICP-MS) is a relatively new method of analysing nanoparticles, which allows for accurate and repeatable measurement of both nanoparticle size and concentration; since the majority of other analytical techniques can measure one or the other variable, SP-ICP-MS has great diagnostic potential; however the technique has yet to be developed fully in order to provide routine analysis of unknown samples containing nanoparticles. To date, the majority of development work has focused on single composition of a handful of reference nanoparticles (gold, silver or titania). Our work involves exploring detection of less well studied or compositionally more complex nanoparticles.

More specifically, we will be presenting data on the characterization of core-shell and doped nanoparticles. The project aims to develop an ability to detect both size and composition of nanoparticles with a core-shell or complex chemistry, first by working out the mathematical and physical requirements that will underpin detection and then studying model systems in more detail. The model systems we are currently working on are: 1) core-shell Au@Ag nanoparticles and 2) hafnium doped ceria nanoparticles. We anticipate our work will enable us to acquire a greater level of detail in the characterization of complex nanoparticles than using other methods such as microscopy and DLS.

Monday, August 15, 2016
Poster Session I
A-104

Asymmetric flow field-flow fractionation as a tool for detection and characterization of TiO₂ and Fe₂O₃ particles in sunscreen

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Many of the sunscreens on the market present a complex matrix containing different engineered particles (e.g. TiO₂ as UV-filter and Fe₂O₃ as pigment). In order to detect and completely characterize engineered particles in a complex matrix of sunscreen (hereafter referred to as complex sunscreen) a multidimensional method for nanoparticle analysis would be required. In the framework of the research project NanoDefine (FP7 - G. A. Nr. 604347-2) the sample preparation method and possibility of using asymmetric flow field-flow fractionation (AF4) hyphenated to multi-angle laser light scattering (MALLS) and inductively-coupled plasma mass spectrometry (ICP-MS) as a tool for detection, quantification, and characterization of engineered nanoparticles (ENPs) in complex sunscreen was tested and evaluated. The sample preparation procedure was evaluated by pre-defined quality criteria, which are mass recovery (calculated by elemental analysis) and change in particle size distribution. The separation of TiO₂ and Fe₂O₃ particles from the complex sunscreen was achieved by a combination of ultracentrifugation and subsequent hexane washing with sufficiently high recoveries, as well as without significant alteration in the particle size distribution. AF4-MALLS-ICPMS analysis after stabilization of isolated TiO₂ and Fe₂O₃ particles indicated that AF4 hyphenated to MALLS and ICP-MS is highly capable for selective on-line detection of TiO₂ and Fe₂O₃ particles and further presents a very important tool in determining ENPs in complex matrices, such as cosmetics.

Monday, August 15, 2016
Poster Session I
A-105

Tracking Nanoparticles in the Aquatic Environments in Taiwan

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To enable environmental risk assessment of nanoscale pollutants, the information regarding the nanoparticle concentrations across environmental compartments is urgently needed. In Taiwan, the semiconductor manufacturing industry is the major driver in the regional economy. Chemical mechanical planarization (CMP) process involved in semiconductor manufacturing uses a large amount of nanoparticle (NP) slurries usually containing SiO₂, CeO₂, and/or Al₂O₃ NPs that are discharged into the waste treatment systems after use before releasing into the receiving waters. The polishing process could also produce nanoscale fragments from the wafers. In this project, we aimed to survey a range of nanoparticles relevant to industrial and consumer usages such as CeO₂, Al₂O₃, ZnO, TiO₂, Au, and Ag across industrial and municipal wastewater treatment plants in Taiwan using single-particle ICP-MS (spICP-MS). We hypothesize that industrially relevant NPs such as CeO₂ are more abundant in wastewater samples from industrial parks than those in municipal wastewater samples. Our preliminary result indicates that CeO₂ NPs were detected in the CMP wastewater effluents with a size between 20 to 25 nm and particle number concentration at ~3000 particles/mL. In this talk, the changes in sizes and particle number concentrations across the treatment trains will also be presented.

Monday, August 15, 2016
Poster Session I
A-106

Composite particle characterization using single particle ICP-MS and field flow fractionation

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Sundiata Kly and Matthew G. Moffitt at University of Victoria, Ronald Lankone and D. Howard Fairbrother at Johns Hopkins University, and James F. Ranville at Colorado School of Mines

As the nanotechnology industry continues to expand with production of a multitude of useful nano-enabled consumer and industrial products, release of engineered nanoparticles (ENPs) into the environment is inevitable. The development of new nano-metrology to quantify (mass, particle number concentration) and characterize (size, composition, aggregation state) ENPs is essential to assessing their impacts and risks to human health and the environment upon their release. Numerous challenges exist for applying these techniques to real-world samples; in some cases, one important issue is a potentially composite structure. This study focuses on composite particles resulting from heteroaggregation and the formation of coatings, which can occur during: release from nano-enabled products, biological uptake, or environmental transport. A methodology using a combination of TEM, spICP-MS, and/or FFF was employed to characterize two complex composite particles representing a) heteroaggregation and b) particle release from polymer nanocomposites. TEM provides a traditional, visual observation and particle sizing method. spICP-MS provides the inorganic NP size and particle number concentration based on elemental mass. Two FFF techniques, asymmetric flow field-flow fractionation (AF4) and centrifugal field-flow fractionation (CFFF), separate and size particles based on their hydrodynamic size and buoyant mass, respectively. The first composite particle is a heteroaggregate model consisting of SiO₂ NPs (several hundred nm in size) with smaller Ag NPs (<100 nm) attached to the surface. spICP-MS provided the ratio of SiO₂-mass:Ag-mass for two different Ag-SiO₂ NP batches; these results were compared to the TEM data. The second model particle, representing composite particles released from nano-enabled products due to material weathering or abrasion, consists of one or more Au NPs (approximately 40 nm in size) surrounded by a thick polystyrene-polyacrylic acid block copolymer (PS-b-PAA) shell (up to about 150 nm thick). spICP-MS demonstrated the presence of multiple Au NPs incorporated inside the PS-b-PAA shell, consistent with TEM results. Separation by AF4 and CFFF and spICP-MS analysis of fractions showed that the average number of incorporated Au NPs (i.e., Au mass) increased with increasing hydrodynamic size, and provided the Au mass distribution with increasing incorporated Au mass. This methodology has potential uses in industrial manufacturing processes, monitoring release of ENPs

into the environment from the use and disposal of NEPs, and assessing transformations of ENPs in the environment.

Monday, August 15, 2016
Poster Session I
A-107

Quantifying cerium oxide nanoparticles using spICP-MS with microsecond dwell times

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Dr. Manuel Montañ o, Duke University; Dr. Steve Anderson, Duke University;
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The increasing use of engineered cerium oxide nanoparticles (CeO₂ NPs) necessitates an accurate method for quantitation and characterization of these NPs. As CeO₂ NPs inevitably enter the environment, it is important to understand their fate, dictated by degree of aggregation and subsequent sedimentation. Current nanometrology techniques are either imprecise or implausible, inhibiting further investigation into the environmental burden of CeO₂ NPs. Quantitation techniques, like traditional Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), are imprecise when applied to environmental matrices due to interferences of background cerium. Optical sizing techniques, such as microscopy or light scattering, fail to determine NP size in a complex aquatic matrix, are not scalable to environmental sampling, and may unintentionally alter the samples prior to analysis. spICP-MS allows for the direct analysis of an aquatic sample without altering its chemistry, and measures both particle concentration and particle size distribution of the NPs. To further improve this method, we employed shorter dwell times (0.1 ms), or discrete intervals of detection. Short dwell times allow us to better distinguish between the noise of background cerium from particles and analyze samples at environmentally relevant concentrations. Using 0.1 ms spICP-MS, we analyzed three CeO₂ NPs from different manufacturers and distinct categorical diameters, ranging between ~10 and 300 nm. To investigate this method's robustness in environmental conditions, we applied it to the unfiltered water of wetland mesocosms which were dosed with the small and large NPs. In both cases, we were able to precisely quantify particle concentration and their respective sizes. The consistency of data exhibited in these experiments, especially in natural aquatic conditions, highlights the promise in spICP-MS in understanding CeO₂ environmental fate and behavior.

Monday, August 15, 2016
Poster Session I
A-108

Nanomaterials Characterization: State of the Art, Challenges, and Emerging Technologies

Chady Stephan, PerkinElmer

Nanomaterials characterization is complex and requires many analytical platforms in order to achieve the task at hand. This talk connects nanomaterials parameters that most commonly need to be measured with corresponding measurement techniques. It is a brief overview for nanotechnology scientists to rapidly identify the appropriate technique needed for measuring nanomaterials. Among the techniques that will be discussed;

Single Particle ICP-MS is a new advancement in ICP-MS devoted to the analysis of individual metallic nanoparticles ranging from single digit nm up to a few μm . It is element specific, allows the differentiation between ionic (M^+) and particulate signals (particles) in a wide variety of matrices without any prior separation. In one sample analysis, SP-ICP-MS provides ionic and particle concentration, particle composition, size and size distribution.

Direct Sampling Analysis (DSA) Time of Flight (TOF) mass spectrometer is an ambient ionization technique coupled to an accurate mass spectrometer allowing the analysis of capping agent. The organic capped ligands are released from the nanoparticles due to thermo-lability of the covalent bonds. Using accurate mass and isotope profile information provided by the TOF, we were able to confirm the presence of the different types of ligands attached to nanoparticles. Besides just identifying and confirming one type of organic monolayer covalently bound to the nanoparticle, we were also able to identify bilayers wherein, one organic monolayer is covalently modified with a second type of organic ligand.

Thermal Gravimetric Analysis (TGA) "Infra Red (IR)" Gas Chromatography Mass Spectrometry (GC/MS) is a very powerful combination of analytical techniques all operated together in synergy towards the identification of various organics residing on the surface of Nanostructure.

Monday, August 15, 2016
Poster Session I
A-109

Modification of the toxicity of Ge-imogolite nanotubes due to tube wall defects

Armand Masion, CNRS-CEREGE
A. Avellan, C. Levard, J. Rose, C. Santaella

The influence of structural modifications on NM toxicity, and in particular structural defects, is poorly studied mainly because of the difficulty to modify the crystallinity of a NM without changing any other morphological parameters. In this study we used a singled-walled alumino-germanate nanotube (Ge-imogolite) as a model, for which this can be achieved. Well crystalized tubes led to moderate toxicity attributed to a direct contact with the bacteria and the generation of reactive oxygen species, whereas lacunar tubes caused more severe toxic effects without any direct contact nor ROS generation. The bacterial growth inhibition in the presence of wall defects was attributed to indirect mechanisms as their higher solubility leading to Al or Ge ion toxicity and/or to the retention of essential nutrients on the vacancies.

Monday, August 15, 2016
Poster Session I
A-110

Response surface methodology (RSM) to obtain desired aggregate size of carbon nanotubes in water by sonication

Qammer Zaib, Masdar Institute of Science and Technology

Carbon nanotubes tend to aggregate in water due to non-specific hydrophobic forces and substantial van der Waals attractions. A molecular dynamics study calculated 28.66 kJ/mole increase in free energy when carbon nanotubes are moved from air to water. This positive change in free energy, contributed by carbon-carbon and water-water interactions, makes the aqueous dispersion of carbon nanotubes (thermodynamically) unfavorable. Therefore, external energy is required to disperse them which is usually provided by mechanical tools like rotor stator mixers, colloid mills, ball mills, shear mixers, and sonicators. Sonication is the extensively used mechanical dispersion technique primarily due to its simplicity of application. It reduces the size of carbon nanotube aggregates, shortens their length, opens their ends, and grafts the functional groups to their sidewalls and terminal ends. This alteration in morphology of carbon nanotubes increases their hydrophilicity and enables them to better disperse in water. However, a great risk of carbon nanotube integrity damage is also associated with improper sonication due to the occurrence of complex physical and chemical phenomena during the process. If not accounted for properly, these phenomena lead to adversely alter the characteristics of carbon nanotubes in dispersion. Unfortunately, less attention is paid to this apparently simple process of sonication, which often results in frequent occurrence of 'under-sonication' and/or 'over-sonication' of carbon nanotube dispersions. The inadequate dispersion and/or breakage of carbon nanotubes during sonication is a one such example.

A process for optimizing sonication parameters in order to obtain multiwalled carbon nanotube (MWNT) dispersions of required aggregate size (mean diameter and standard deviation) is developed. MWNTs were dispersed in water with the aid of a probe sonicator under different sonicator operational settings (parameters/ variables/ factors) of sonication time, amplitude, and pulse mode to observe their effects on mean diameter and distribution (standard deviation) of MWNT aggregates. The model was developed, analyzed, and validated to predict the dispersion of MWNTs at different sonicator parameters. Finally, desired range of sonicator parameters were identified for a set criterion of minimizing size and variability of carbon nanotubes bundles at minimal sonication energy cost.

Tuesday, August 16, 2016
Poster Session II
A-201

Improved nanotube synthesis by the use of micro-waves

Armand Masion, CNRS-CEREGE
A. Avellan, C. Levard, C. Chaneac, J. Rose, F. Onofri

The synthesis of Imogolites nanotubes is a simple aqueous sol-gel process, consisting in a partial hydrolysis of a mixture of Al and Si (or Ge) monomers followed by a growth step requiring at least 5 days of heating. Here we describe an alternate way of obtaining these nanotubes by substituting conventional heating in an oven with micro-wave heating. Tubes were obtained within the hour. When applying micro-waves during 2 hours, the tubes precursors were absent from the suspension and the size distribution of the tubes was shifted by one order of magnitude towards higher aspect ratios. The underlying mechanisms causing this improved synthesis are discussed.

Tuesday, August 16, 2016
Poster Session II
A-202

Biological and Environmental Media Control Oxide Nanoparticle Surface Composition: The Roles of Biological Components (Proteins and Amino Acids), Inorganic Oxyanions and Humic Acid

Vicki Grassian, UC-San Diego

Developing nanotechnology in a sustainable way requires fundamental understanding of how nanomaterial properties affect their reactivity, environmental fate, and toxicity in a range of environmental and biological media/systems. It is well known that nanoparticle surfaces have high free energy and therefore thermodynamic driving forces will work toward minimizing the surface energy. In order to achieve a lower energy state, nanoparticles undergo different physical and chemical transformations including surface reconstruction, aggregation, dissolution and ligand adsorption. In environmental or biological systems, the surrounding milieu will drive these interactions. Therefore it is important to consider nanoparticles as dynamic entities that undergo rapid transformations that depend on solution pH, ionic strength and composition. A focus of this talk will be to highlight a few examples of in situ characterization of oxide nanoparticle surfaces in different environmental and biological media so as to show the importance of the milieu on surface composition. The surface composition is shown to be vastly different in different media with adsorption of biological components (proteins, peptides and amino acids), inorganic oxyanions and humic acid occurring. The extent of surface adsorption depends on the solution phase composition and the affinity of different components to adsorb to the nanoparticle surface as will be discussed. For protein adsorption, it will be shown that the secondary structure changes with biologically and environmentally relevant pH and for different types of oxide nanoparticles. As will be discussed, protein-nanoparticle interactions are strongly dependent on pH and specific nanoparticle-surface interactions.

Tuesday, August 16, 2016
Poster Session II
A-203

High Resolution ICP-MS in single particle mode as a powerful technique for measuring very small metal nanoparticles

Madjid Hadioui, University of Montreal

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As the production and use of various types of nanoparticles (NPs) increases significantly, the need for analytical tools allowing their detection and accurate characterization is becoming essential. Due to their size and high surface area, the very small nanoparticles (below 10 nm) are expected to show the greatest interaction and reactivity with (micro)organisms in the environment. Hence, there is a great need for extremely sensitive tools that will allow the detection of very small NPs at environmentally relevant concentrations. Among the available techniques, single particle ICP-MS (SP-ICPMS) is a promising tool that is still under continuous development. For instance, almost all of the reported studies on single particle ICP-MS have involved quadrupole mass filters and detectors with a sensitivity that does not allow the detection of nanoparticles smaller than ca. 13 nm (for silver and gold NPs). Size detection limits are even higher for some metal oxide NPs (ca. 30 nm). In this work high resolution ICP-MS was used to analyze Ag and CeO₂ nanoparticles with particle sizes in the range of 5 - 10 nm. Short dwell times (20 to 100 μ s) were investigated along with wet (concentric nebulizer with a Peltier cooled glass cyclonic chamber) or dry (membrane desolvation system) sample introduction. When samples were injected as wet aerosol, size detection limits as low as 6.0 nm and 3.5 nm were determined for Ag and CeO₂ NPs, respectively, which resulted from a gain in sensitivity of ca. 33 times for Ag and 31 times for Ce, when compared to a standard quadrupole ICP-MS. In the case of dry sample introduction, an even higher (> 8 times) transport efficiency was obtained, resulting in a greater gain in sensitivity for dissolved analyte (ca. 19 times higher). When using the dry conditions and enhanced sensitivity cones, an relatively small gain in ion extraction was noted for the nanoparticles, which resulted nonetheless in a decrease in the size detection limits (down to 3.3 nm and 2.9 nm, for Ag and CeO₂, respectively), and the attainment of a lower background signal (with no significant effect on particle size distributions).

Tuesday, August 16, 2016
Poster Session II
A-204

Determination of multi-element composition and mass of single nanoparticles in liquids and air

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The list of analytical techniques which can be applied for nanoparticle detection in complex media and at low environmentally relevant concentrations (ppt-ppb) is very short and for most of the studies complementary approaches are considered. Single particle (sp)-ICP-MS provides an easy and routinely applied way to quantitatively determine size and number concentration of metal-containing nanoparticles. Moreover, element-specific detection makes sp-ICP-MS more tolerant to high levels of natural background (e.g. organic matter, bacteria).

Along with size and concentration, multi-element composition of single nanoparticles is extremely valuable to study chemical transformations of particles once they have entered the real ecosystem. Besides, composition of single particles can be used as a specific merit for the identification of synthetic nanoparticles in the presence of naturally occurring particulate background and for particle source tracing. The TOFWERK icpTOF mass spectrometer allows for detection and quantification of all isotopes in single particles.

In this study we compare different methods for quantification of elemental composition and mass of single particles in both aqueous media and in air using the icpTOF. Standard sample introduction was used for liquid sampling. For air sampling, we coupled a recently developed gas exchange device (GED) to the icpTOF in line with the metal standard gas generator (MSGG). Calibration was realized using element standard solutions and either MSGG or Au standard nanoparticles from NIST. Different calibration approaches were validated using synthetic nanosteel particles in water and urban particulate matter from NIST suspended in air. The feasibility of the technique was demonstrated for outdoor and indoor air samples, car exhaust, and smoke samples.

Tuesday, August 16, 2016
Poster Session II
A-205

A Highly Stable and Reusable Hybrid nano Iron Catalyst and for Environmental Application

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A novel approach of Low temperature mediated chemical reduction was followed to obtain Nano-Sized Carboxymethyl Cellulose-(Fe²⁺-Fe⁰) Hybrid [nCMC-(Fe²⁺-Fe⁰)]. The stepwise formation mechanism of Nano iron hybrid was discussed in detail and evaluated with advanced instruments. The resultant Nano iron hybrid was characterized using UV-Vis spectrometer, Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS) and high resolution transmission electron microscopy (HR-TEM). The oxidation reduction properties of Nano iron hybrid was demonstrated with cyclic voltmeter (CV) measurement. The reactivity of resultant particles was evaluated using phenol as the model pollutant. Catalytic property of nano iron hybrid was evaluated using phenol as a model pollutant. Reusability study was performed for used nano iron hybrid catalyst.

Tuesday, August 16, 2016
Poster Session II
A-206

**Nano-particle analysis using dwell times between 10 μ s and 70 μ s
with a detection limit of less than 10nm for Ag and Au.**

Ariane Donard, Nu Instruments
Phil Shaw

Inductively coupled plasma mass spectrometry (ICP-MS) is proving to be a useful tool for characterization and quantification of metallic nanoparticles. However, the short (150 - 400 ns) transient signals generated by single particle events present challenges to current ICP-MS instrumentation. Minimum dwell times are available now in the 50-100 μ s timings but limitations in sensitivity for quadrupole ICP-MS make analysis of smaller particles difficult below 50 μ s.

This work will present data acquired with dwell times down to 10 μ s for a range of nanoparticles. The advantages of the higher sensitivities possible with the Nu AttoM will be demonstrated. We will describe the unique detection system of the AttoM which can measure fast transient signals to $>10^7$ cps. We will also describe an additional range extension facility based on physical attenuation of the ion beam which allows the same faster dwell times to be used for signals in excess of 10^9 cps.

High signal to noise detection of 10nm particles will be demonstrated along with the ability to display and process nanoparticle data within the Nu Quant data processing package. The flexible capabilities of NICE scripts (Nu Instrument Calculations Editor) to customise the processing and reporting of particle numbers and sizes will be shown with the charting capability to report multiple distributions from a single data collection. The data processing methods allow easy discrimination of 15nm and 20nm particles from significant levels of ionic background signals with graphical and tabulated reports available for particle size, particle concentration, ionic concentration, detection limits, calibrations and size distributions with normal and log-normal fitting.

Tuesday, August 16, 2016
Poster Session II
A-207

CHARACTERIZATION OF TiO₂ NANOPARTICLES AS FOOD ADDITIVE

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Titanium dioxide (TiO₂) is a white metal oxide commonly used as a white pigment in various applications such as paints, cosmetic but also food products where it constitutes the coating of sweets and chewing-gum. Due to the classification of TiO₂ nanoparticles as potentially harmful for humans by inhalation, the toxicity after ingestion raised concerns and needs to be evaluated. However, the physicochemical characteristics of food grade TiO₂ are poorly known. In this study, we studied several food grade TiO₂ samples (size distribution, shape, crystallinity, reactivity, surface properties) and evaluated whether they are similar to the well-known P25 particles that served as reference for numerous toxicological studies. The main result of our study is that E171 and P25 are different particles, with different compositions and surface chemistry. TEM analysis confirmed the presence of nanoparticles in P25 and in E171 samples, but the primary sizes and the percentage of nano-sized particles were different: 23 nm with 100% of nanoparticles in P25 and 131 nm with 26% of nanoparticles in E171. Isoelectric points were assessed by zeta potential measurements and were determined at pH 6.2 for P25 and between pH 2 and pH 4.2 for E171 depending on suppliers. Particle size distribution analyses showed different agglomeration behavior: E171 tended to form larger agglomerates at pH < 5 whereas P25 formed larger agglomerates at pH > 5. XRD, XPS, FT-RAMAN, DRIFTS, surface specific area analysis and ICP-AES analysis showed P25 particles are a mixture 75/25 of rutile/anatase with a pure and reactive surface, whereas E171 is a 100% anatase, coated with some organic impurities, and sometimes silicon and aluminum. Finally, this work confirms the recent paper of Yang et al., 2014 (Environ. Si. Tech. 2014, 48, 6391) and provides some more data on food grade TiO₂ surface chemistry including specific surface area and DRIFTS measurements but also size distribution evolution from pH 1 to pH 9. Some variability was also found among food grade TiO₂ samples, leading us to strongly recommend researchers to properly characterize their samples before each of their toxicological studies. In any case, using Degussa P25 particles does not appear to be the most reliable model to study the fate of food grade TiO₂ in the gastro-intestinal tract.

Tuesday, August 16, 2016
Poster Session II
A-208

PIXE ANALYSIS OF GROUNDNUT GENOTYPES FOR TOXIC ELEMENTS

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Concentrations of Elements in nine selected groundnut genotypes have been analyzed by means of PIXE (Particle Induced X-ray Emission) practice with an interior standard method to search traces of remaining agricultural chemicals or toxic elements in selected groundnut genotypes in Accelerator lab National Center for Physics Islamabad. We arranged the samples by separating seed of the groundnut into two cotyledons (seed leaves). The cotyledon recorded many elements but recorded none of the toxic element such that Pb, Hg, As and Cd. The peanut seeds used in the present amount are concerned.

Tuesday, August 16, 2016
Poster Session II
A-209

Evaluating the Effect of Engineered Nanomaterial Surface Coatings on Aggregation Processes in Aquatic Environments

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Worldwide, engineered nanomaterials (ENMs) are increasingly being used in consumer goods, such as paints, plastics, and cosmetics. However, the potential environmental risks associated with ENMs has come under scrutiny in the U.S. and other nations. Due to the nature of their use, ENMs can enter natural surface water environments, such as lakes, rivers and estuaries, via point sources (e.g., effluent from wastewater treatment systems) and non-point sources (e.g., overland flow from soils amended with ENM-containing biosolids). Recent modeling efforts indicate that the environmental fate of ENMs in natural aquatic environments is tied to their potential to aggregate with other ENMs (homoaggregation) and natural colloids (heteroaggregation). By affecting the environmental fate of ENMs, these dynamic and complex interactions can in turn alter the potential risk posed by ENMs. To-date, the mechanisms governing these interactions are poorly understood. One challenge researchers face is to understand how engineered surface coatings, typically applied to ENMs to promote a desired behavior during their use, can alter those interactions. To address this challenge, this research looks at the role that common surface coatings have upon ENM stability (i.e., the ability to resist aggregation) under complex, environmentally relevant conditions. Aggregation of ENMs coated with various functionalized forms of polyethylene glycol and branched polyethylenimine (bPEI) were assessed in a range of environmentally relevant conditions; e.g., pH 6-10 with varying ionic strengths and ion valence, as well as in the presence of natural organic matter (NOM). Initial findings suggest that the surface coating can play a significant role in ENM stability across a wide range of aquatic chemistries. For example, results show that bPEI can stabilize ENMs in high ionic strength solutions. However, in the presence of NOM, bPEI-coated ENMs were found to aggregate at conditions typical of natural waters. In addition, research is underway that investigates the interactions of ENMs in more complex environments that mimic freshwater, estuarine, and marine waters that include the presence of natural colloids (e.g., silica and hematite) and NOM. This research will focus on assessing the role that ENM surface coatings on ENM heteroaggregation processes (i.e., interactions between ENMs and natural colloids) and how the presence NOM may influence those interactions.

Tuesday, August 16, 2016
Poster Session II
A-210

Bioavailability-based separation of natural nanoparticles at environmentally-relevant concentrations using AF4 coupled to quadrupole ICP-MS under metal-free, ultra-clean conditions with advanced quality control

Chad Cuss, University of Alberta
Iain Grant-Weaver, William Shotyk

The toxicity of natural nanoparticles is a function of their speciation: mainly ionic, 'truly dissolved' species are the most toxic, colloids may be toxic under some circumstances, and large aggregates or particles with encapsulated metals are generally inert (e.g. Pb inside iron oxyhydroxides). Such size-based 'speciation' of engineered nanomaterials is also important since large aggregates, suspended 'colloidal' species, and dissolved ions exhibit differing levels of toxicity. Until recently, methods for determining the speciation of dissolved metals have suffered from interferences (e.g. potentiometry) or high detection limits that are not environmentally relevant (e.g. ion-selective electrodes). While field-flow fractionation is capable of separating dissolved species by size, it remains challenging to measure trace metals at the low concentrations prevalent in surface waters. Detecting engineered nanomaterials in the environment is similarly challenging, since they are found at concentrations well below those of natural nanoparticles. This poster will report on the development and application of online asymmetrical flow field-flow fractionation (AF4) coupled to inductively coupled plasma mass spectrometry (ICP-MS) with absorbance detection for separating dissolved organic and metallic nanoparticles into bioavailability-based fractions at environmentally-relevant concentrations. Differences in the distribution of dissolved species in several waters will be presented. The importance of conducting analyses under in-situ conditions by tuning the AF4 eluent will be demonstrated by showing the shifts in speciation that can be caused by relatively minor shifts in pH. We will also outline the specialized equipment, procedures, and quality control measures used to ensure the lack of contamination, high reproducibility (e.g. Mp of Suwannee River NOM \pm 95% CI = 986 ± 6 Da, $n = 5$), lack of carryover, and low detection limits necessary to measure environmentally-relevant concentrations using a quadrupole ICP-MS (e.g. 0.2 ng L⁻¹ Pb).

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-301

Concentration dependent dissolution behavior of PVP-coated silver nanoparticles in seawater

Mithun Sikder, University of South Carolina
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Dissolution is an important environmental transformation process for silver nanoparticles (Ag NPs), which affects their size, speciation, bioavailability fate and transport in natural water systems. Here we investigated the dissolution of sterically stabilized PVP-coated Ag NPs in synthetic seawater (i.e. 30 parts per thousand.) to enable the controlled evaluation of Ag NP dissolution in the absence of aggregation. Dissolution was measured by monitoring the release of Ag ions from Ag NPs surfaces, the loss in PVP-Ag NPs absorbance, and the reduction in NP size as a result of ion release. Inductively coupled plasma-mass spectroscopy (ICP-MS) was used to quantify Ag ion release, ultraviolet-visible spectroscopy (UV-vis) was used to monitor optical properties of Ag NPs in seawater, and atomic force microscopy (AFM) was used to monitor NP size distribution over a 96 hour period. The percentage of dissolved Ag concentration relative to initial Ag NPs concentration measured by ICP-MS and UV-vis followed the same trend and increased with time; however, UV-vis overestimated the % of dissolved Ag ions. This discrepancy was corrected by taking into account the reduction in NP extinction coefficient caused by the reduction in their size. Finally, dissolution of Ag NPs at variable concentration (25-1500 μgL^{-1}) was monitored by UV-vis. Results demonstrate that Ag NPs dissolve faster and to a larger extent, consistent with the measured decrease in NP concentration. Additionally, with the decrease in NP concentration dissolution rate increased exponentially.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-302

Stability of Gold Nanoparticles in Simulated Lysosomal and Cytosolic Environments

Jared Bourget, Colorado Mesa University

Joe Delaney is an additional author and professor Sam E. Lohse is the research adviser.

Gold nanoparticles (AuNPs) have a wide range of application; from electronics to medical diagnostics. Determining the stability of AuNPs in biological systems is particularly important in informing the design of safer and more effective nanotherapeutics. AuNPs are prone to aggregation (the merging of individual NPs into larger structures) in many biological fluids, which diminishes their effectiveness as therapeutics in many cases. The purpose of this research was to determine and assess the stability of various AuNPs under experimental conditions which simulated lysosomal and cytosolic environments. 12 nm Citrate-stabilized methoxy polyethylene glycol (mPEG) and 11-mercaptopundecanoic acid (MUDA) functionalized AuNPs were exposed to artificial lysosomal fluid (ALF) for several hours, and changes in the stability of the AuNPs were assessed using absorbance spectroscopy and light scattering techniques. The stability of the AuNPs was investigated both before and after the functionalized AuNPs were incubated in serum. When comparing the relative stability of these AuNPs, the stability of citrate-stabilized and mPEG-AuNPs were not significantly different. However, MUDA AuNPs aggregated immediately in ALF when the nanoparticles were not wrapped with FBS. If the particles were incubated in fetal bovine serum first, the AuNPs all showed improved stability in the ALF.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-303

Determining aggregation behavior and corresponding surface reactivity of copper oxide nanoparticles using a rapid colorimetric assay

Lauren Crandon, Oregon State University
Fan Wu, Arek M. Engstrom, Stacey L. Harper

The ability to predict interaction with abiotic or biotic surfaces in complex systems would enhance understanding of the life cycle of nanoparticles (NPs) and assist in evaluation of risk. The aggregation behavior of NPs is a key process determining fate, transport, and bioavailability and is dictated by environmental interactions. In this study, we propose a method to evaluate NP homoaggregation and heteroaggregation, as measured by changes in surface reactivity. In order to observe NP reactivity, methylene blue dye is used as a chemical probe which is reduced by sodium borohydride in the presence of a NP catalyst. The resulting color change is observed with ultraviolet-visible spectrophotometry. We hypothesized that the rate of reaction is directly related to the NP aggregation state. Copper oxide (CuO) NPs were selected as a model NP in this study due to their widespread industrial and commercial applications and high reactivity. The relative reactivity of 1 mg/L CuO was evaluated after CuO NPs were allowed to either homoaggregate for 2 and 24 hours or heteroaggregate with green algae *Chlorella vulgaris* for 24 hours. The reaction rate did not significantly decrease after 2 hours of homoaggregation. However, the rate significantly decreased by almost 100% after 24 hours homoaggregation compared to non-aggregated CuO NPs, and by 34% when CuO NPs were heteroaggregated with algae cells. The decrease in reaction rates was likely due to a decrease in overall NP reactive surface area. The surface area of the CuO NPs stock suspension was calculated using nanoparticle tracking analysis. This method allows us to rapidly and efficiently assess both surface reactivity and agglomeration and can be applied to environmentally relevant complex suspensions.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-304

Interaction of Nanoparticles with Model Gram-Negative and Gram-Positive Bacterial Surfaces

Emily Caudill, University of Wisconsin-Madison

Emily R. Caudill¹, Joseph T. Buchman², Hilena Frew³, Kyle P. Johnson³, Marco D. Torelli¹, Christy L. Haynes², Z. Vivian Feng³, Robert J. Hamers¹, Joel A. Pedersen¹ ¹University of Wisconsin-Madison; ²University of Minnesota; ³Augsburg College

Bacteria are ubiquitous in terrestrial and aquatic environments and play integral roles in ecosystem functions. The interaction of bacteria with nanomaterials released into such environments may elicit adverse effects or result in the transformation of nanoparticles. One of the primary modes of adverse nanomaterial interaction requires contact with the bacterial cell surface. Our objective is to determine the critical chemical components of Gram-negative and Gram-positive bacterial cell surfaces that govern their interaction with nanoparticles. We used diamond nanoparticles functionalized with the cationic polymer poly(allylamine hydrochloride) as a model system for a nanoparticle with an inert core and positively charged surface. We have employed complementary spectroscopic, imaging, and in situ monitoring techniques to study the interaction of these nanoparticles with model Gram-negative and Gram-positive cell surfaces. We constructed model Gram-negative bacterial cell surfaces containing lipopolysaccharides and find that type and amount of lipopolysaccharides significantly impacts the extent of nanoparticle attachment. To study nanoparticle interaction with Gram-positive bacterial surfaces, we isolated so-called sacculi, which consist of peptidoglycan and covalently attached wall teichoic acids (anionic glycopolymers). Preliminary solid-state NMR results suggest that positively charged diamond nanoparticles associate with wall teichoic acids. We expect that our results will ultimately inform the assessment of risks posed by nanomaterials released to the environment, as well as nanoparticle manufacturing to modulate interactions with Gram-negative and Gram-positive bacteria.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-305

Concentration-dependent aggregation of citrate-coated silver nanoparticles: Role of cystine

Kamelia Afshinnia, University of South Carolina
Dr. Mohammed Baalousha (Assistant Professor, University of South Carolina)

Cystine is widely used in cell culture media. Cysteine, the reduced form of cystine is widely used to differentiate dissolved vs. NP uptake and toxicity. However, still little is known about the effect of cystine and cysteine on aggregation behavior of silver nanoparticles in particular as a function of AgNPs concentration. In this study, we investigated the effect of cystine on the stability of citrate-, polyvinylpyrrolidone-, and polyethylene glycol- coated silver nanoparticles (cit-Ag NPs, PVP-Ag NPs and PEG-Ag NPs, respectively) in the presence and absence of Suwannee River fulvic acid (SRFA) as a function of AgNPs concentration (ca. 125-1000 $\mu\text{g L}^{-1}$). The results indicated for the first time the concentration-dependent aggregation of AgNPs in the presence of cystine. Critical coagulation concentration (CCC) shifted to lower cystine concentrations at lower cit-Ag NP concentrations. No CCC was measured at the highest cit-Ag NP concentration (1000 $\mu\text{g L}^{-1}$) and reaction limited aggregation (RLA) was only observed. Also, no CCC value was measured in the presence of SRFA and aggregation of cit-Ag NPs by cystine in the presence of SRFA only occurred in RLA regime. Cystine replaces citrate, PVP and PEG coatings, resulting in aggregation of both electrostatically and sterically stabilized Ag NPs. These findings play a key role in understanding the uptake and toxicity of Ag NPs vs. Ag ions suggesting that the reduced toxicity of Ag NPs in the presence of cysteine could be due to a combined effect of scavenging Ag^+ ions and Ag NP aggregation.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-306

Method development for the characterization of titanium dioxide and zinc oxide nanoparticles in commercial sunscreens

Jin-Hee Lim, FDA/ORArkansas Regional Lab
Venu Gopal Bairi, Andrew Fong

There has been a tremendous increase in the usage of sunscreens due to concerns about UV exposure. Along with organic UV-absorbers, inorganic minerals such as nanoscale TiO₂ and ZnO are also often employed in a majority of commercial sunscreens. The toxicity of these nanoparticles is not completely understood in humans and environment. There is an immediate necessity for developing analytical techniques for the isolation and characterization of nanoparticles in sunscreens. Since sunscreens contain up to 75% of a variety of organic materials, isolation of these mineral particles from sunscreens is quite challenging. This study was focused on the isolation of nanoparticles using several different techniques such as extraction with various solvents, plasma ozonolysis and filtration. Among all of the isolation techniques, extraction with tetrahydrofuran solvent was found to be the most effective for isolation of mineral particles from sunscreen products. The extracted samples were analyzed using electron microscopy (TEM and SEM), energy-dispersive X-ray spectroscopy, dynamic light scattering, disc centrifugation, UV-Visible spectroscopy and X-ray diffraction techniques. The extract contains a mixture of both TiO₂ and ZnO, therefore bulk size characterization technique such as DLS and CPS are problematic. Elemental analysis along with electron microscopy proved to be a valuable technique for individual identity of nanoparticles.

Improvement of the nanoparticle size limit of detection for SP-ICP-MS using a desolvating nebuliser to improve both sample transport and ion transport efficiencies and pseudo resolution to remove interferences with the HR-ICP-MS AttoM.

Phil Shaw, Nu Instruments
Ariane Donard

Engineered nanoparticles are regularly being used in a multitude of industrial products. The release of these substances into the environment and the questions raised about a potential harm for the human health require the development of methodologies to characterise those materials over the range of anticipated sizes and concentrations present in-situ. SP-ICP-MS has been proven in recent years to be a useful tool for particle counting, sizing and quantification. The HR-ICP-MS AttoM allows the acquisition of data with a dwell time down to 10 μ s, (with no settling time). The combination of fast signal acquisition capacity, high sensitivity and the ability to remove interferences by physically separating the ions at a resolution high enough to distinguish the analyte from the interference make the AttoM a promising instruments for this technique. In this work, the capability of this instrument demonstrates the improved limit of detection achievable with the use of a desolvating nebuliser or high resolution to resolve interferences.

Due to its high ion transmission efficiency, the AttoM already reaches low limits of detection for SP-ICP-MS in conventional nebuliser and spraychamber introduction mode (6 nm for Au, Ag, CeO). In this work, the use of a desolvating nebuliser improves these limits of detection further (4 nm for Au, Ag, CeO). The data collected allows for a distinction between sample transport efficiency and ion extraction efficiency, this is compared to understand the increase in sensitivity seen and the fundamentals of this type of nebuliser.

The resolution capacity of the AttoM was also used for the size measurement of two nanoparticle types for which the isotopes measured have polyatomic interferences (Cr_2O_3 and Fe_2O_3). The ability to independently control of source and collector slits is demonstrated, allowing resolution whilst maintaining the benefit of the classical flat top peak from the Nier-Johnson mass spectrometer geometry. This technique allows for greater stability for static on peak measurements free from interference with less reduction in sensitivity compared to full resolution. The limits of detection reached for interfered nanoparticles will be discussed.

Matrix Effects and validation of Single Particle ICP-MS for Measuring Nanoparticle Size and Size Distribution

Antonio Montoro Bustos, NIST

Single particle inductively coupled plasma mass spectrometry (spICP-MS) is considered an emerging and promising analytical technique for the ultrasensitive detection and characterization of metal-containing nanoparticles (NPs). Particularly, spICP-MS offers exceptional potential for providing information about particle size and size distribution, agglomeration/aggregation state, and particle number concentration, at mass concentration levels down to ng L⁻¹.

However, despite its highly valuable utility, some important limitations still remain, and spICP-MS cannot be considered a mature methodology. Validation of the technique for measuring NP size and size distribution is required before it can be properly applied for sizing and quantifying NPs. The main limitation to validation is the near total lack of NP test specimens having reliable reference information.

This communication explores the usefulness of high-resolution scanning electron microscopy (HR-SEM) as a reference technique for spICP-MS size validation by using NIST reference material (RM) gold nanoparticles (AuNPs). This approach has also been applied for an extended and statistically significant size characterization of several coated commercial AuNPs whose mean size and size distribution information provided by the supplier is limited to the analysis of only 100 NPs.

Further, the capabilities of spICP-MS for the quantitative evaluation of the influence of different coatings on the stability of AuNPs are evaluated. It is expected that the information attainable by spICP-MS could offer a better understanding of the role of the coating in the behavior of AuNPs in suspension at environmentally relevant concentrations.

During this evaluation, an important matrix effect in the ionization and/or nebulization of the NPs in the plasma is observed, even though highly diluted NP samples are required for spICP-MS measurements. If the matrix interferes with the nebulization or ionization in the ICP-MS plasma, leading to suppression or enhancement of the analyte signal, an underestimation or overestimation of particle concentration and particle size would result. The novel concept of "matrix-specific" transport efficiency will be presented to compensate the matrix influence on spICP-MS providing accurate particle size

and particle concentration results and extending the validity of spICP-MS results to a large range of aqueous, environmental and biological conditions.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
A-309

Development of Thermal Field-Flow Fractionation for the Characterization of Compositional Dispersity in Metal Hybrid Nanoparticles

William Smith, Colorado School of Mines

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Thermal field-flow fractionation (ThFFF) is developed for the separation and characterization of metal hybrid nanoparticles by composition. Unlike asymmetrical flow field-flow fractionation which utilizes a crossflow "field", ThFFF utilizes a temperature gradient to invoke a different and intriguing separation mechanism. In addition to translational diffusion, analytes can also undergo thermal diffusion (usually from higher temperature to lower temperature regions). The interplay between the thermal diffusion coefficient DT and the translational diffusion coefficient D has a key role in determining the equilibrium position of different analytes in the parabolic flow profile of the ThFFF channel.

Their relationship to the observed retention time t_r and the temperature drop applied across the channel ΔT is given by: $t_r = (\Delta T \cdot DT) / D$

All parameters in the above equation are known except for D and DT . An average D value can be determined using batch-mode dynamic light scattering (DLS) or alternately, the DLS can be coupled to ThFFF to provide on-line D measurement of eluting components. Once D is known, DT can be calculated. The magnitude of DT has been demonstrated to be sensitive to polymers and nanoparticles of different compositions.

The specific nanoparticle system investigated in this work is Pt, Fe₃O₄, and Pt-Fe₃O₄ metal hybrid nanoparticles (MHNp). MHNPs are of increasing interest because of their multiple functionalities and synergistic properties and if introduced into large scale use, will present a currently unmet analytical and environmental challenge. ThFFF-DLS analysis of Pt and Fe₃O₄ NPs in organic solvent yielded different DT values which were used to establish the boundary values of a composition calibration plot. The measured DT for Pt-Fe₃O₄ MHNp lay between the values for the single component particles and are correlated to the mass percent of each constituent component. Online DT determination combined with concentration detection offers quantification of compositionally distinct particle subpopulations and enables the evaluation of polydispersity in both particle size and composition. Composition distributions constructed from online DT values represent the first measurements of its kind for these complex

hybrid nanoparticles. The observed composition sensitivity of ThFFF shows promise for the characterization of other hybrid nanoparticle systems.

Release, Fate, and Applications

Oral Presentations



Monday, August 15, 2016
Release, Fate, and Applications I
9:30 AM

Environmental and biological transformations of emerging two-dimensional nanomaterials beyond graphene

Robert Hurt, Brown University
Zhongying Wang, Evan Gray

The isolation of graphene by exfoliation in 2004 has now led to the new field of two-dimensional materials. Inorganic 2D materials â beyond grapheneâ have now become a major focus in materials research worldwide with substantial efforts centered on synthesis, characterization, and technological application. These high-aspect-ratio sheet-like solids come in a wide array of chemical compositions, crystal phases, and physical forms, and are anticipated to enable a host of future technologies in areas that include electronics, sensors, coatings, environmental barriers and selective membranes. This work focuses on the environmental and biological behavior of the broad class of emerging 2D materials beyond graphene. We start by considering stability and dissolution, which affect persistence, fate, transport, biokinetics, device stability, and toxicity mechanisms. A thermodynamic screening analysis is presented that predicts that many 2D materials will undergo either oxidative or reductive dissolution processes in biological systems and the natural environment. This analysis is tested by experimental data for MoS₂ nanosheets as a case study, which exhibit a 2H semiconducting phase and a 1T metallic phase depending on the method of exfoliation. The 1T phase undergoes a well-defined oxidation in aqueous media by dissolved dioxygen under ambient conditions accompanied by nanosheet degradation and release of soluble molybdenum and sulfur species. The oxidation generates protons that can also colloiddally destabilize the remaining sheets. The oxidation kinetics are pH-dependent, and a kinetic law is developed and proposed for use in biokinetic and environmental fate modelling. The semiconducting 2H phase oxidizes at much slower rates, and mixed-phase materials are seen to gradually transform from 1T/2H to pure 2H due to preferential oxidation of the 1T component. The environmental applications and implications of MoS₂ oxidation and nanosheet degradation will be discussed.

Monday, August 15, 2016
Release, Fate, and Applications I
9:50 AM

Fabrication and characterization of multi-walled carbon nanotube-based membrane flow sensors for water treatment

Marielle DuToit, Duke University

Unique flow sensors integrated into water filtration membranes have been fabricated using multi-walled carbon nanotube (MWCNT) films as the active sensing elements. The sensing device consists of a MWCNT film coated onto the surface of a polymeric filtration membrane, which is placed in a cross-flow filtration cell outfitted with electrical leads that connect to a control circuit. The conductive membrane is heated with an electrical current; as fluid flows through the membrane, heat is carried away, which causes the electrical resistance of the hot MWCNT film to change. In this design, the membrane behaves like a variable thermistor within a Wheatstone bridge circuit. Small variations in resistance are translated into voltage signals and amplified within the circuit. The MWCNT film simultaneously improves filtration performance by conferring desirable anti-fouling properties to the membrane. Finally, electrical and thermal analyses have been conducted to determine the temperature coefficient of resistance, thermal conductivity, sensitivity and frequency response of the device.

Monday, August 15, 2016
Release, Fate, and Applications I
10:10 AM

Unraveling the Complexity in the Aging of Nano-Enhanced Textiles: a Comprehensive Sequential Study on the Effect of Sunlight, Washing and Landfilling

Denise Mitrano, EMPA

Enzo Lombi (University of South Australia, Centre for Environmental Risk assessment and Remediation); Yadira Arroyo Rojas DaSilva (Empa, Swiss Federal Laboratories for Materials Science and Technology, Electron Microscopy Center); and Bernd Nowack (Empa, Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory)

The potential for nanomaterials to be released from consumer goods is not in itself a new topic, but the basis of scientific understanding of released particles and the transformations they may undergo during the products life cycle (e.g. during storage, use and disposal) is often hampered by the narrow scope of many research endeavors in terms of both the breadth of variables studied and the completeness of characterization using multiple analytical methods. Additionally, studies of sequential aging of products representing multiple stages of the life cycle are scarce. In order to bridge these gaps for the release of nanomaterials from textiles, we conducted a comprehensive suite of studies which allowed us to suggest some overarching themes for finding important mechanisms and parameters for particle transformations when still adhered to the fabric or when released. Laboratory prepared nano-enhanced fabrics were subjected to sequential combinations of sunlight irradiation, washing (in seven different detergent formulas, in 1 or 10 wash cycles) and simulated reactive landfilling. Characterization is divided into two groups: analysis of solutions (washing and landfill leachate) and analysis of the NP fraction that remained on the fabric. Analytical techniques included single particle spICP-MS and TEM of the released particles, fabric digestion and total metal analysis after each exposure scenario, and both SEM and XANES analysis of the textiles for the visual integrity and speciation of Ag, respectively. Some broad generalizations suggest that sunlight irradiation hinders further speciation upon washing (as suggested by XANES). More Ag is released from fabrics than Au suggesting additional chemical influences and while a size effect may also be in play, the capping agent plays the largest role. However, when release does occur, a large proportion of particles are released into the wash water with little to no alteration of the size compared to the primary particle size (as determined by sp-ICP-MS). As seen in our previous work, detergent chemistry plays a significant role in concentrations of Ag released, where those containing oxidizing agents clearly assist in release of Ag particles (but not Au NPs, again inferring the additional chemical reactions specific to Ag). This undertaking of a large matrix of variables makes us more confident to make more overarching characterizations since

trends can be monitored across more variables than in any other nano-composite release study to date.

Monday, August 15, 2016
Release, Fate, and Applications I
10:30 AM

Tiered Testing of Nano-TiO₂ Release Potential from Self-cleaning Concrete Under a Modeled Scenario

Alan Kennedy, US Army Engineer Research and Development Center
Alan J. Kennedy*, Stephen A. Diamond#, Aimee R. Poda*, Charles A. Weiss*,
Jr., Jonathon Brame*, Kevin Torres-Cancel*, Nicholas Melby*, Tahirih Lackey*,
Daniel Harrison, Robert D. Moser*; *US Army Engineer Research and
Development Center, Vicksburg, MS

TiO₂ is one of the highest production volume nanomaterials. Its application in self-cleaning concrete provides a relevant in-use release scenario during construction and weathering of infrastructure. The known UV-photoreactivity of TiO₂ is purported to "depollute" concrete surfaces by oxidizing NO_x and SO_x and photocatalyzing soot and other organic compounds. TiO₂ may enter the environment during production, transport, use, and weathering of concrete. While the aquatic toxicity of TiO₂ is low relative to other nano metals, UV-light induced formation of reactive oxygen species dramatically increases toxicity. In this investigation, a published tiered testing framework was used to design release, fate and hazard experiments. The release scenarios included runoff during construction, in addition to abrasion and weathering of cured concrete in a solar simulator. To determine hazard during construction, data were generated in presence and absence of UV light using *Ceriodaphnia dubia* to compare the toxicity of a free TiO₂ surrogate (Evonik P25) and a self-cleaning concrete mix (TX Active). Weathered (UV exposed) and abraded particles were collected from cured concrete pucks to determine potential releases from finished concrete infrastructure. Portland cement (no TiO₂) was comparatively tested. Imaging of the abraded self-cleaning concrete revealed nano to micron sized TiO₂ occurring as isolated aggregates embedded in cementitious particles. Photocatalytic degradation of fluorescent dyes demonstrated that the abraded self-cleaning concrete retained phototoxicity. While P25 was 86% anatase, the self-cleaning concrete TiO₂ was nearly 100% anatase. The toxicity of P25 increased 70-fold under UV illumination, from a lethal median concentration of 2.54 to 0.03 mg/L. All concrete materials induced alkaline conditions in biological test media, and was neutralized using HCl prior to testing. The 2% TiO₂ content of the self-cleaning concrete did not result in substantially greater phototoxicity relative to Portland Cement. To estimate environmentally-relevant exposure, a construction scenario (4,000 lbs concrete/yd³; 5% waste) near Cleveland Harbor was used to populate the Army Corps Particle Tracking Model (PTM). Future work will improve TiO₂ phototoxicity dose response relationships and calibrate PTM for nanoparticles (agglomeration, attachment, etc.).

Monday, August 15, 2016
Release, Fate, and Applications I
11:20 AM

Release of Nanoparticles from Surface Coatings: Is this really Nano exposure?

Todd Luxton, US EPA

Justin G. Clar, Elon University; William Platten, US EPA Office of Water; Eric Baumann, Pegasus Technical Services; Treye Thomas, US Consumer Product and Safety Commission

Continued research in nanoscience and nanotechnology has resulted in a variety of "nano-enabled" products currently available for consumer purchase. A major area of growth for these consumer products has been the inclusion of engineered nanoparticles (NPs) in surface coatings including paints, stains and sealants. NPs have been added to these products to increase their UV protection, scratch resistance, hydrophobicity, etc. Two NPs of particular interest are cerium oxide (CeO₂) and zinc oxide (ZnO) as they have been widely included in paints and stains to increase UV resistance. In this study, both Micronized-Copper pressure treated lumber, and a commercially available composite decking were coated with extensively characterized CeO₂ and ZnO NPs dispersed in Super-Q Water or wood stain. Additionally, a suite of commercially available wood stains and sealants, advertised as containing ZnO nanoparticles, were applied to Micronized-Copper pressure treated lumber. Coated surfaces were allowed to weather outdoors for a period no shorter than 6 months. During weathering, periodic sampling of the surface was completed using a modified method developed by the Consumer Product Safety Commission to estimate the release of NPs from the surface through dermal transfer. The total concentrations of Ce, Zn and Cu released throughout weathering was tracked through ICP-OES. The form of released material (particle versus ion) was determined through sequential filtration and X-Ray Absorption Fine Structure Spectroscopy. Our results indicate that both the surfaces used in coatings, as well as the matrix used in NP dispersion has a dramatic impact on the potential for release.

Monday, August 15, 2016
Release, Fate, and Applications I
11:40 AM

Eco-design of Sunscreen Using titanium dioxide Nanoparticles

Jerome Labille, CNRS CEREGE

J. Labille, D. Slomberg, J.-C. Hubaud, L. HÃ©douin, S. Motellier, I. Capron

Among cosmetics and personal care products, sunscreen products are of emerging concern regarding both human and environmental health. The fate and impact of mineral nanoparticulate UV-blockers, such as TiO₂ nanomaterials, is under consideration from a regulatory perspective due to their potential impact. Once leaving the skin either through bathing or everyday usage and cleaning, the nanomaterials contained in the sunscreen can be released into rivers, lakes, sea shores, and/or sewage treatment plants. The nanomaterial behaviour, fate and impact in these different systems is largely determined by its surface properties, (e.g. the nanomaterial coating type) and lifetime.

Here we present the first result of the Eco-SUN research program aimed at developing the eco-design of sunscreens through the minimization of risks associated with nanomaterials incorporated into the formulation. Different stages of the cream lifecycle are considered from its manufacture to its end of life, through its use by the consumer and its impact on the exposed environments. Reducing the potential release and / or toxicity of the nanomaterial from the cream is a decisive criterion for its eco-design.

Different relevant TiO₂ UV-blockers have been selected to integrate a typical w/o formulation as case studies. The resulting sunscreens were characterised in terms of nanomaterial localisation, sun protection factor and photo-passivation. The risk for the consumer by dermal exposure will be assessed using skin biopsies. Inflammation and skin penetration will be evaluated.

The risk for the aquatic environment directly exposed was assessed both in terms of exposure and hazard. The release of nanomaterials from the sunscreen upon normal usage was studied in laboratory through simulated aging procedure. Two biological models, sea urchin and coral colonies, were selected as relevant endpoints to assess the marine ecotoxicity of the byproducts formed.

Finally, the risk related to the end of life of the sunscreen through the removal with cleaning water followed by drainage to sewage treatment plants will be evaluated by considering two opposite fate scenarios: (i) nanomaterial concentration in sewage sludge later spread as fertilizer in agriculture, and (ii) nanomaterial suspension maintained in the treated water and released in river water. Thus, fate and impact in soil and river ecosystems will also be studied.

Tuesday, August 16, 2016
Release, Fate, and Applications II
11:20 AM

Investigation of the Paris city contribution to CeO₂ Nanoparticles and TiO₂ Nanoparticles in the Seine River by spICPMS and FEG-SEM imaging

Marc Benedetti, Institut de Physique du Globe de Paris
Univ. Paris Diderot

A field investigation was made along the Seine River watershed from upstream to downstream Paris city to survey the occurrence of two engineered nanoparticles (NPs): CeO₂ and TiO₂. single particle Inductively Coupled Plasma-Mass Spectroscopy (spICPMS) [1] and Field Gun Emission-Scanning Electron Microscopy (FEG-SEM) were applied on the river water samples to detect and characterize these NPs. In the Seine River water, Ce and Ti particle number concentrations increase from upstream to downstream of Paris city. The highest particle number concentration was found in the Marne River, a tributary of the Seine River, with 1.60×10^6 part mL⁻¹ and 6.00×10^6 part mL⁻¹ for Ce and Ti, respectively. This influences the NPs concentrations measured downstream the Marne and Seine rivers confluence, where it increases up to 1.40×10^6 part mL⁻¹ and 4.70×10^6 part mL⁻¹ for Ce and Ti, respectively. Another increase was observed 11 km downstream the Paris city, near a waste water treatment plant (Bougival) where 1.20×10^6 Ce-bearing part mL⁻¹ and 4.60×10^6 Ti-bearing part mL⁻¹ were detected. FEG-SEM imaging confirmed the occurrence of both Ti- and Ce-bearing particles, with sizes ranging from 0.2 to 5 μ m in the suspended matter isolated from the water samples.

Tuesday, August 16, 2016
Release, Fate, and Applications II
11:40 AM

Measuring nanoparticle release from nanocomposites in the natural environment

Ronald Lankone, The Johns Hopkins University Dept. of Chemistry
Robert Reed (2), Katie Challis (2), David Hanigan (3), Yuqiang Bi (3), Yan Wang (4), Jiaoyang Yin (4), Mike Garland (5), Teri Dankovich (6), Greg Lowry (6), Robert Tanguay (5), Leanne Gilbertson (4), James Ranville (2), Howard Fairbrother (1), 1) The Johns Hopkins University, 2) Colorado School of Mines, 3) Arizona State University, 4) University of Pittsburgh, 5) Oregon State University, 6) Carnegie Mellon University

Over the last year, we have coordinated the installation and operation of outdoor weathering stations in five locations across the continental United States - Baltimore, Md. Tempe, Az. Golden, Co. Pittsburgh, Pa. and Corvallis, Or. - with the explicit goal of measuring both nanoparticle release and local weather conditions at each location. Samples are setup to weather and release nanoparticles passively, with no artificial agitators (sonication, wiping of the surface, rinsing with surfactant, etc.) applied to induce release. Carbon nanotube polymer nanocomposite (CNT-PNC) and silver nanoparticle polymer nanocomposite (AgNP-PNC) are the principle materials of interest in this study. Samples were prepared in lab (via solution blending), and characterized for their initial surface morphology (scanning electron microscopy), chemical composition (x-ray photoelectron spectroscopy), and chemical structure (attenuate total internal reflectance-IR). Nanocomposites were placed in custom designed sample holders on rooftops at each location; nanoparticle release in the accumulated rain runoff was collected and measured on a monthly basis with inductively coupled plasma mass spectrometry (ICP-MS). The total release measured was complemented by local weather data in the form of temperature, precipitation, solar fluence, and UV index. Samples were again characterized following exposure. More recently, commercially available micronized copper azole (MCA) treated lumber was included for weathering as well. Release from the MCA lumber was measured with the same approach as used for the PNCs (in both weathering setup and characterization scheme) to assess the role that climate plays in regulating nanoparticle release. Collectively, information from these studies will inform more accurate life cycle assessment models and assess the kinetics of nanoparticle release. Future work aims to expand the variety of samples to be weathered and develop experimental methods to allow for both toxicity measurements of released material and identification of the released materials' functional form (i.e. individual nanoparticles vs. nanoparticle/polymer fragments).

Tuesday, August 16, 2016
Release, Fate, and Applications II
12:00 PM

Quantifying emissions and environmental risks of cemented carbide (WC) nanoparticles from tire studs

Anna Furberg, Chalmers University of Technology
Assistant professor Rickard Arvidsson and Professor Sverker Molander, both from the division of Environmental Systems Analysis at Chalmers University of Technology

Tire studs, with pins typically made out of cemented carbide (WC), are used in several countries to improve the gripping power during winter. Throughout their use, the tire studs are worn. This leads to emissions of particles, of which some are nano-sized. Until now, WC nanoparticles have seldom been included in environmental risk assessments of nanomaterials. The aim of this study is to assess the magnitude of emissions of WC (nano)particles from tire studs on a national level, compare WC emissions to those of other nanoparticles, and conduct a screening risk assessment of the WC emissions. The country in focus was Sweden, where 64% of the passenger cars use studded tires during winter. Substance flow analysis (SFA) was used to quantify the mass flows related to tire studs from the raw material extraction phase to the waste management phase. Furthermore, particle flow analysis (PFA) was used to quantify particle number flows in the use phase, where emissions of WC nanoparticles have been observed. As part of these quantifications, use phase emissions of WC nanoparticles were calculated using a leaching-type model based on the number of km driven by the Swedish car fleet and experimental measurements of WC emission rates. Two scenarios 'a low-emission and a high-emission scenario' were employed. Preliminary results show annual WC emissions of $10\text{-}10^3$ kg/year and $10^{15}\text{-}10^{20}$ particles/year. These estimated emissions were then compared to estimated emissions of some other nanoparticles in Sweden, including silver, titanium dioxide, cerium oxide, fullerenes and carbon nanotubes. This comparison indicated that the emissions of WC nanoparticles from tire studs are in the same range as estimated emissions of some of these other nanoparticles. Our estimation of the predicted environmental concentration (PEC) of WC nanoparticles in road runoff was in the same order of magnitude as measured environmental concentrations (MEC) of W-containing particles. The limited existing ecotoxicity data indicate that much higher concentrations are required in order to reach toxic levels, but further studies are needed to confirm this. Overall, the notable emissions of WC nanoparticles during the use of tire studs support the further study and inclusion of this material in risk-related studies of nanoparticles.

Tuesday, August 16, 2016
Release, Fate, and Applications II
1:50 PM

Comparison between Chemicals and Nanomaterials: Characterization of Pristine and Transformed Nanoparticles from Foods and Personal Care Products

Paul Westerhoff, Arizona State University
David Hanigan, Pierre Herckes, Jared Schoepf, Justin Kidd, Yuqiang Bi (and
others)

Nanomaterials are often used as a replacements for organic chemicals in a wide range of products. This presentation examines two case studies where this is occurring: 1) nanoscale needle-shaped hydroxyapatite (HA) used as a calcium supplement in infant formula, and 2) nanoscale titania and zinc as sunblock in personal care products. While pristine needle-like shaped HA is facing banning in cosmetics in the EU, and cell assays suggest these HA shapes induce toxicity, we find that this shape rapidly dissolves in gastric fluids. Thus it would appear that pristine HA differs significantly in impact over transformed nanoparticles for the intended purpose of delivering soluble calcium in the gut of infants. The second example will compare organic chemical alternatives (e.g., oxybenzone) and nanoscale alternatives for sunscreens. Both provide the intended function (reduced skin cancer risk), and we will discuss recent toxicity work using zebrafish embryo and environmental impacts of both chemical and nanoforms in the water column. Complimenting the themed discussion will be introduction of new, rapid screening methods to detect the presence of some nanoparticles in complex matrices such as foods and personal care products.

Tuesday, August 16, 2016
Release, Fate, and Applications II
2:10 PM

Testing the effect of aging and dissolution on the extractability of Cu from CuO-NPs amended soil to assess lability and fate in soils.

Xiaoyu Gao, Carnegie Mellon University

Due to a growing interest in fertilizers and pesticides using metal and metal oxide nanoparticles in agriculture, there is a need for understanding how such nanoparticles behave in agricultural soil. So far, the link between metal and metal oxide nanoparticles' transformations in soil, particularly dissolution processes and their bioavailability is not fully understood. The objectives of this research were to assess the effect of aging and dissolution on lability of CuO-NPs from extractability of Cu in soil dosed with CuO-NPs and Cu(NO₃)₂ using 0.01M CaCl₂ and 0.005M DTPA (pH 7.6) extraction methods along 31 days. We performed these extractions at selected time points to determine how aging of the ions or particles affects their extractability. The dissolution of CuO-NPs was inferred from the changes in the speciation of Cu in soil using X-ray absorption spectroscopy. For soils dosed with 100 mg Cu Kg⁻¹ dried soil CuO-NPs or Cu(NO₃)₂, there was marked differences in the amount of extractable Cu. At the maximum, CuO NPs was ~50% less extractable than the Cu from Cu(NO₃)₂. The temporal trends for DTPA- and CaCl₂-extractable Cu from CuO-NP amended soil were very different than for Cu(NO₃)₂-amended soil. For high dose (100ppm) DTPA extraction, CuO NPs' extractability increased with time from a 3wt% right after mixing to 38wt% after 31 days. For Cu(NO₃)₂ amended soils, Cu extractability decreased over time from ~95wt% right after mixing, to ~80 wt% after 31 days. The increase in extractability of CuO-NPs in soil with time was due to its slow dissolution of, as inferred from changes of speciation from CuO to Cu-Humic acid observed by X-ray absorption near edge structure. Our findings suggest that dissolution and aging are the key factors controlling CuO-NPs' bioavailability in soil, and suggest that test guidelines to predict bioavailability will need to consider time as a test variable.

Tuesday, August 16, 2016
Release, Fate, and Applications II
2:30 PM

Quantification of dermal exposure to nanoparticles from solid nanocomposites by using single particle ICP-MS

Aiga Mackevica, Technical University of Denmark
Mikael Emil Olsson, Steffen Foss Hansen, Technical University of Denmark

Engineered nanoparticles are used in various applications due to their unique properties, which has led to their widespread use in consumer products. Silver, titanium and copper-based nanoparticles are few of the most commonly used nanomaterials in consumer products, mainly due to their biocidal, optical or photocatalytical properties. There is a lot of research focusing on effects exerted by nanoparticles, but the knowledge concerning release and subsequent exposure to nanoparticles is very limited, and information regarding potential dermal exposure from nanomaterial containing solid articles in particular is currently lacking. Challenges with regard to qualitative and quantitative characterization of nanoparticle exposure have been increasingly addressed in the literature in the last decade, and single particle ICP-MS has shown to be one of the most promising techniques for nanoparticle detection and characterization.

In this study, we have investigated the potential dermal exposure to three different types of nano-enabled consumer products: Ag-containing keyboard covers, TiO₂ coated ceramic tiles, and wood painted with CuO containing paint. The potential for dermal transfer from the aforementioned surfaces was tested by surface wiping followed by analysis using single particle ICP-MS. The nanoparticles were extracted from the wipes by ultrasonication in deionized water, and this technique was tested to be around 60-100% effective for extracting the particles adsorbed to the wipes. The method was optimized by spiking the wipes with known amounts of nanoparticles and treating them the same way as the experimental samples. Our preliminary results show that single particle ICP-MS has the potential for quantitatively measuring potential dermal exposure to nanoparticles, and when used in combination with other characterization techniques, such as conventional ICP-MS (for analysis of total metal content) and electron microscopy (particle shape) it can provide necessary particle characterization that can aid consumer exposure assessment to nanoparticles.

Tuesday, August 16, 2016
Release, Fate, and Applications II
2:50 PM

Release of plasticizers and polymer additives from carbon nanotube enabled composites

Manuel Montano, Duke University

Ronald Lankone (Johns Hopkins University, Department of Chemistry), Howard Fairbrother (Johns Hopkins University, Department of Chemistry), Lee Ferguson (Duke University)

The rapid development of nanotechnology in recent decades has led to an explosion of nano-sized materials with unique properties. Many of these unique nano-enabled properties make these materials attractive as filler materials for polymer and plastic composites. Carbon nanotubes (CNTs) in particular exhibit unique optical, electrical, thermal, and mechanical that make them ideal candidates for incorporation into plastics and polymer composites. With the continued manufacture of nano-enabled materials, it is highly likely that the components of nano-enabled composites will be released into the environment through use and disposal. Where many studies have focused on the potential release of engineered nanomaterial from these nano-enabled products, few have focused on the potential for nanomaterial to affect the release and behavior of molecular contaminants similarly liberated from nano-enabled composites. In this study, polycarbonate, BADGE, and BFDGE composites were prepared with varying levels of carbon nanotube mass loadings to investigate the release of plasticizers and polymer additives under environmentally relevant conditions. Concentrations of bisphenol A, BADGE and BFDGE monomer were quantified by LC-MS/MS through a 48hr exposure period in EPA moderately hard water and TCLP extraction media to simulate potential environmental release scenarios. Other potential exposure scenarios such as elevated temperature and UV exposure were also investigated. At room temperature, little release of bisphenol A was exhibited from the nano-enabled composites; however, at elevated temperature (45 oC) a considerable amount of bisphenol A (20-200 ppb) release was demonstrated. Preliminary results from single particle ICP-MS show that little CNT release is shown during the 48-hr time period. Additional experiments aim to incorporate fluorescent CNTs into the composites to allow for CNT quantification by near-infrared fluorescence spectroscopy. Though the development of nano-enabled composites show considerable promise, it will be important to ascertain an understanding of not only the inherent ecotoxicological potential of nanomaterials, but how they might also influence the biological and environmental stressors present in the environment.

Tuesday, August 16, 2016
Release, Fate, and Applications II
3:10 PM

Fate of nanomaterials for Life Cycle Impact Assessment: combining the USEtox and Simple-Box4Nano models.

Beatrice Salieri, EMPA

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The Life Cycle Assessment (LCA) methodology is widely applied to assess the environmental and human potential impact of chemicals. To date only few LCA studies on Nano Materials (ENMs) have been carried out, among others due to the gap of knowledge on fate, exposure and toxic effects. For the assessment of the toxicological impact, the USEtox model is seen as the default fate-exposure-effect model for organic and inorganic chemicals, but is still not suitable for ENMs. The present project aims to expand and adapt the USEtox model in order to model fate and exposure of ENM in the environment. To achieve this objective, we combine the principles of the recent, nano-specific fate multimedia model SimpleBox4Nano with the USEtox framework, defining three subcompartments - to describe the masses of free, aggregated and attached ENMs in each media. The fate of ENM in air, freshwater, soil, and sediment environmental media is first evaluated at steady-state by including the nano-specific fate processes (aggregation, attachment), calculated as first order kinetics. Similarly to the original USEtox model for organic substances, the here proposed "USEtox-SimpleBox4Nano" multimedia fate model provides the fate of ENMs expressed in term of rate constant (day⁻¹). We then extend the approach to propose a dynamic version of the "USEtox-SimpleBox4nano" model to study the time to reach steady state. The developed model is tested and applied to several type of ENMs, ranging from metal oxide nanoparticles (i.e. nano-TiO₂) to Carbon-based materials (i.e Fullerene).The result -i.e. for an emission of free nano-TiO₂ in air- the steady state in air is quickly reached at 1.0E+00 day, whereas in water sediment, soil the steady state for the free, aggregated and attached nano-TiO₂ is reached in range of order from 1.0E+01 to 1.0E+06 day. Once emitted in air the free nano-TiO₂ are quickly removed to soil where they get attached to soil's solid grain; here the slow process of erosion is the mainly removal process which occurs and thus, the steady state is reached at 1.00E+06 day for nano-TiO₂ attached to solid in grain in soil.

This work is of great relevance in view of the development of a methodology in the area of LCIA for a sound and adequate assessment of human and toxic impact of releases of ENMs.

Thursday, August 18, 2016
Release, Fate, and Applications III
2:50 PM

Transformation of nanoparticulate cerium oxide diesel fuel catalyst during combustion, and aspects of its potential environmental interaction

James Dale, Virginia Tech
Marina Vance, Amy Dale, Amalia Turner, Steve Cox, Linsey Marr, Michael F. Hochella, Jr.

Nanoparticulate cerium oxide (n-ceria) is the active ingredient in the commercial diesel fuel catalyst Envirox™, and its transformation induced by combustion in an engine was studied using high resolution transmission electron microscopy (HR-TEM) and a variety of bulk analytical techniques. The 5 to 7 nm cerium oxide faceted single crystals found in Envirox™ are predominately released as 50 to 300 nm single crystal spheroids of cerium oxide in the exhaust. Electron diffraction of the emitted particles confirmed that they were cerium (IV) oxide (CeO₂) single crystals, but further investigation revealed the presence of superlattice reflections. These reflections most closely resemble a CeO₂ structure containing ordered oxygen vacancies. The emitted particles typically did not have a coating, though in approximately 30% of the particles analyzed, a coating of 2 to 5 nm thickness was observed. Energy dispersive X-ray spectroscopy (EDS) indicated that several particles contained Ca and Al impurities, though EDS mapping showed that these impurities were not localized within the particles and no systematic variations to the particles were observed. On two occasions, 250 to 300 nm aggregates composed of 50 to 70 nm cerium oxide crystals were found, likely representing stages of incomplete formation of larger particles.

The cerium oxide emitted into the environment from the use of Envirox™ likely has significantly different properties from the particles contained in the additive; these differences would include airborne transport, surface reactivity, and long-term behavior due to size, shape, surface coatings, and internal defects. It is unlikely that a monodisperse, laboratory-prepared n-ceria will model environmental interactions accurately. Currently, this lab is undertaking experiments which involve the modeling of atmospheric transport of the released cerium and the exposure of exhaust material containing cerium oxide to *Brassica napus* (dwarf rapeseed). Atmospheric modeling predicts the most significant increases in cerium concentration to be within 20 m of roadways and to be up to tens of ppm per year. Preliminary plant exposure experiments indicate that there is no significant impact on the growth of the plants exposed to cerium-bearing exhaust, but there is a systematic increa!

se in the concentration of cerium in the roots of exposed plants. Cerium does not appear to be significantly translocated into the above ground biomass of the plant.

Thursday, August 18, 2016
Release, Fate, and Applications III
3:10 PM

Engineering metal oxide nanomaterials for enhanced disinfection of viruses

Kelvin Gregory, Carnegie Mellon University
Brian E. Vencalek and Gregory V. Lowry

Transmission of pathogenic waterborne viruses through the fecal - oral route continues to present a serious threat to populations lacking adequate water and wastewater treatment infrastructure. For these populations, point-of-use (POU) water treatment methods may be a viable, short-term alternative for preventing outbreaks of waterborne illness. However, many of these POU technologies do not remove viruses and an additional disinfection step is required before water is safe for consumption. Recent developments in nanotechnology suggest that engineered nanomaterials possess several qualities desirable for removing viruses from drinking water. While previous studies have characterized the antibacterial properties of metal and metal oxide nanoparticles, comparatively fewer have characterized their antiviral properties, representing a significant knowledge gap. Nano -scale materials are expected to provide an attractive compromise between the high reactivity of ionizable salts and the stability of bulk phase metals for use in contact disinfection systems. Of the transition metals, copper (Cu) is of particular interest due to its relatively low cost and established use as a disinfectant capable of inactivating viruses. Hypothetical mechanisms of virus disinfection with CuO nanoparticles and nanoparticle aggregates include sequential adsorption and inactivation, with Cu²⁺ ions catalytically degrading H₂O₂ and producing ROS and unstable Cu species via Haber-Weiss and Fenton-like reactions at the virion-NP interface. Ongoing research indicates that CuO nanoparticles can rapidly achieve significant rates of virion disinfection (> 4 log removal) in the presence and absence of H₂O₂. Moreover, the release rate of the toxic metal ion species can be controlled by optimizing the primary particle size to provide an extended release source of Cu²⁺ ion sufficient to achieve log 4 inactivation without exceeding drinking water standards. Ongoing experiments seek to identify and exploit nano-specific disinfection mechanisms.

Thursday, August 18, 2016
Release, Fate, and Applications III
3:50 PM

Implication of Manufactured Nanomaterials to Drinking Water Resources

Endalkachew Sahle-Demessie, US EPA
Changseok Han, Amy Zhao, Heidi Grecsek

As nanomaterials become increasingly part of everyday consumer products, it is imperative to measure their potential release during production, use, and disposal, and assess their impact on the health of human and the ecosystem. This compels the research to better understand how the properties of manufactured nanomaterials (MNMs) lead to their accumulation and redistribution in the environment whether they could become emerging pollutants or can affect the mobility and bioavailability of other toxins. If nanoparticles are released from their matrix, the high surface to volume ratio and reactivity of MNMs makes them highly dynamic in environmental systems. The resulting transformations of the MNMs affect their fate, transport, and toxic properties. Photodegradation of nanocomposites in the environment during the use or end-of-life could release of MNM from the polymer matrix. This study aims in better understanding of polymer physical and chemical properties on the aging process and the human and environmental risks of using consumer products, such as polymer nano-composites. This presentation focuses on the characterization, occurrence in the environment, detection and analysis, toxicity, fate and transport of MNM and the efficacy of water treatment methods in removing them from drinking water supplies.

Thursday, August 18, 2016
Release, Fate, and Applications III
4:10 PM

Nanomaterials Characterization, State of the Art, Challenges, and Emerging Technologies

Chady Stephan, PerkinElmer

During the last decade, the production and use of engineered nanomaterials (ENMs) have experienced a drastic increase, resulting in a potential risk of their release into the environment. Therefore, the study of their impact on the environment becomes crucial. The appropriate ecological risk assessment and management of ENMs in the environment requires quantitative measurements of both exposure and effects that should, ideally, be performed by in situ analysis and give physicochemical characterization. In this talk, I will discuss the analytical challenges that relate to nanomaterials characterization when conducting dose response experiments debating approaches to overcome inconsistency using state of the art two analytical technique Single Cell-ICP-MS and Thermogravimetric Analysis (TGA) for both metallic, metal oxide and carbon based ENM. Single Cell ICP-MS allow the quantification of metal content by individual cell or organism providing information to the uptake of 1, 2, 3 or more particles per organism. Thermogravimetric Analysis (TGA) has been identified as a useful tool to characterize SWCNT, MWCNT uptake by microorganism by way of weight loss analysis of the sample as it is heated at 5 °C/min in air.

Release, Fate, and Applications

Posters



Monday, August 15, 2016
Poster Session I
R-101

TiO₂ nanoparticles release from chewing-gums and candies.

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France

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Titanium dioxide is a metal oxide used as a white pigment in coatings of food products as candies and chewing-gum. Food-grade TiO₂, referred to as E171 in Europe and INS171 in North America, includes a nano-sized fraction, representing less than 44% of the particles. Due to concerns about TiO₂ nanoparticles (NPs) as potentially hazardous, the size of TiO₂ particles released from food products during consumption, and an estimation of the intake of nanoparticles from daily life products as chewing-gums and candies is needed. In this study, the coating of 5 food products (4 chewing-gums and 1 candy) were extracted, and TiO₂ particles were quantified and their physicochemical characteristics (size distribution, shape, crystallinity, chemical composition) were given by TEM, FT-Raman, and ICP-AES. The presence of TiO₂ particles was confirmed by FT-Raman in the coating of food products. After coating separation from the gum, up to 12 mg TiO₂/ g food were detected according to the elemental analysis (ICP-AES). TEM analysis confirmed the presence of nano-sized TiO₂ particles, with a mean diameter of 133±42 nm. Additionally, TEM analysis showed in two chewing-gum samples the presence of hundreds of TiO₂ nanoparticles capped in a carbon matrix, forming large agglomerates up to 1750 nm. Other nanoparticles, such as Ca or Mg/Si compounds were also detected with TEM and ICP-AES analyses, depending on the sweet composition. Our results confirmed the presence of TiO₂ in the coating of food products, up to 12 mg TiO₂ /g of food, with a minor fraction being as nanoparticle (21.8%). Numerous TiO₂ nanoparticles are embedded in the matrix formed by food ingredients. However, TiO₂ nanoparticles could be released during digestion and have different impact on health than taken individually.

Monday, August 15, 2016
Poster Session I
R-102

Non-cytotoxic Quantum Dot-Chitosan Nanogel Biosensing Probe for Potential Cancer Targeting Agent

Tyler Maxwell, University of Central Florida

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Quantum dots (Qdot) biosensors have the ability to provide valuable information to researchers and also deliver cargo inside cells. Heavy metal toxicity can be a problem using Qdots as commonly used Qdots contain cadmium. In this study, we report the design and synthesis of a non-cytotoxic Qdot-chitosan nanogel composite using straight-forward cyanogen bromide (CNBr) cross-linking chemistry. The probe was characterized by spectroscopy (UV-Vis, fluorescence), microscopy (fluorescence, SEM, TEM) and Dynamic Light Scattering. This activatable ("OFF"/"ON") probe contains a core-shell Qdot (CdS:Mn/ZnS) 3-5 nm in diameter. Dopamine is bound to the surface which acts as a model drug and fluorescence quencher. Dopamine capped "OFF" Qdot can react with intercellular glutathione (GSH) which releases the dopamine and turns the Qdot "ON" restoring photoluminescence. The Qdot-dopamine conjugate was then coated with chitosan (natural biocompatible polymer) bound with polyethylene glycol (PEG), fluorescein isothiocyanate (FITC; fluorescent dye) and folic acid (targeting motif). To assess cancer cell targeting, the uptake of the probe was measured on cell lines expressing different folate receptor levels. The cytotoxicity of the probe was evaluated on these cells and was shown to be nontoxic even at concentrations as high as 100 mg/L.

Monday, August 15, 2016
Poster Session I
R-103

Predicting Hydroxyl Radical Production from Irradiated Titanium Dioxide Nanoparticles

Jason Coral, Clemson University
Kitchens, CL, Klaine, SJ

Organism toxicity to titanium dioxide nanoparticles (TiO₂ NPs) has been quantified as a response to nanoparticle concentration. While this is a satisfactory explanation for most toxicants, TiO₂ nanoparticle toxicity is highly dependent on environmental conditions. TiO₂ NPs produce reactive oxygen species (ROS), primarily hydroxyl radicals, upon exposure to UV light in aqueous solutions. Quantifying hydroxyl radical formation during TiO₂ NP exposure and using that as the independent parameter in dose response relationships may better reflect the toxicological impact. Our previous research has established that TiO₂ NP toxic dose to *Daphnia magna* decreases by four orders of magnitude, from 1110 mg/L NPs (48h LC₅₀) under cool white fluorescent tubes to 0.202 mg/L NPs (48h LC₅₀) under ultraviolet lights. This increase in toxicity is due to the production of hydroxyl radicals and the subsequent biological interactions of the hydroxyl radical with the organism. The production of hydroxyl radicals can be influenced by multiple environmental factors such as the contribution of NOM to turbidity, radical quenching and aggregation, and the intensity of UV light. The goal of this research was to characterize the influence of these external parameters on hydroxyl radical formation. Other parameters that were investigated include the following: light intensity and duration, concentration of NOM, and concentration of TiO₂ NPs. Based on measurements from fluorescent spectroscopy, we have built a model that utilizes site-specific water quality and particle specific attributes to better describe the production of hydroxyl radicals generated by TiO₂ NPs. This model will facilitate the development of site-specific water quality criteria for TiO₂ NPs, and is being applied to develop dose-response toxicity curves to *D. magna* based on hydroxyl concentration.

Monday, August 15, 2016
Poster Session I
R-104

Environmental and Economic Optimization of a Nano-Enabled Renewable Energy Portfolio

Elizabeth Wronko, Rochester Institute of Technology
Callie Babbitt, Christy Tyler, Gabrielle Gaustad

Engineered nanomaterials (ENMs) have unique properties that are well suited for emerging technologies, including solar cells, lithium-ion batteries, fuel cells, and supercapacitors. ENMs may enter the environment at any point in their life cycle, creating direct risks to aquatic ecosystems, and indirect impacts from upstream energy and material consumption. It has yet to be fully determined if the potential risks of ENM production and release outweigh the benefits they convey, for instance increasing performance of energy conversion and storage devices. As demand for renewable energy technologies increases, it is imperative to proactively consider future waste generation and potentially hazardous substance releases that may result from increased use of ENMs. To understand life cycle tradeoffs for production-scale ENMs, key questions remain: 1) To what extent will these materials be adopted for various technologies; 2) Where might they be released and in what quantities; and 3) What will the ultimate ecotoxicity be for expected release concentrations? To address these questions, an integrated model was developed: First, @Risk was used to optimize a potential portfolio of ENM adoption in end uses, using a case study of carbonaceous nanomaterials (CNMs) in renewable energy technologies based on energy efficiency performance and marginal cost. Next, a material flow analysis (MFA) was used to model stocks and flows of CNMs contained within renewable energy devices based on the portfolio optimization. Finally, a geospatial analysis was used to demonstrate where these CNM releases may impact aquatic ecosystems based on regional adoption of renewable energy technologies. The examples of CNMs that have been studied include spherical fullerenes (C60, C70), fullerene derivatives such as phenyl-C61 butyric acid butyl ester (PCBM) and indene-C60 bisadduct (ICBA), carbon nanotubes (CNTs), and graphene. The outputs from this integrated model forecast how future adoption may lead to ecological risks. Preliminary results demonstrate that under different scenarios and constraints, ICBA is the optimal material for organic photovoltaic cell (OPV) acceptors with a high efficiency gain and minimized material costs. This poster will provide a detailed overview of the integrated methodology, the key results and recommendations regarding optimized use of CNMs in the future, and the implications of results on future ecotoxicity testing approaches and risk mitigation.

Monday, August 15, 2016
Poster Session I
R-105

Influence of carbon nanomaterial structure on the bioavailability of adsorbed PAHs; a comparison between graphene and carbon nanotubes

Erica Linard, Institute of Environmental Toxicology Clemson University
Peter van den Hurk, Stephen J Klaine

Concurrent with the high applicability of carbon nanomaterials (CNM) in a variety of fields and the potential use for pollution remediation, there is the inevitable release of CNMs into the environment. In the aquatic environment CNMs will interact with natural organic matter (NOM), becoming dispersed and suspended. Due to CNMs' high adsorption affinity for organic contaminants (OC), there is significant concern that CNMs will act as contaminant transporters. Despite this, few studies exist that have quantified the bioavailability of CNM-adsorbed contaminants. Graphene and carbon nanotubes (CNTs) are some of the most commonly used CNMs and while both are made up of a similar carbon lattice, studies have suggested that the physical structure of the adsorbent can influence adsorption behavior, particularly the adsorption of planar molecules such as polycyclic aromatic hydrocarbons (PAHs). Even though adsorption and desorption of contaminants from CNMs play a significant role in the ultimate fate of adsorbed compounds, currently there is little conclusive information characterizing the relationship between adsorption behavior and bioavailability of CNM-adsorbed contaminants. The goal of the present research was to use PAHs as model organic contaminants to characterize the influence of CNM structure on the adsorption of PAHs and how structure relates to the resulting bioavailability of the adsorbed PAHs. Adsorption isotherms of a suite of PAHs to CNTs and graphene were established in conjunction with quantifying the bioavailability of the adsorbed PAH to *Pimephales promelas* (fathead minnow) using bile analysis via fluorescence spectroscopy. Experimental results showed that linear PAHs adsorbed to CNTs and graphene were less bioavailable than angular or bulky PAHs. Further, although graphene had a lower adsorption capacity for linear PAHs compared to CNTs, the PAHs were less bioavailable when adsorbed to graphene over CNTs, which suggests that PAH molecular configuration may play a significant role in bioavailability of CNM-adsorbed PAHs due to alignment with the carbon lattice of CNMs.

Monday, August 15, 2016
Poster Session I
R-106

A biodynamic understanding of dietborne and waterborne uptake of Ag NPs in a sediment-dwelling oligochaete

Stine Tangaa, Roskilde University

Marie-Noele Croteau (USGS, Menlo Park, CA); Margrethe Winther-Nielsen (DHI, Hoersholm, DK); Henriette Selck (Roskilde University, Roskilde, DK)

Metal-containing engineered nanoparticles (Me-ENPs) are used in a wide range of consumer products, such as inks, plastics, lubricants, electronics and bioactive coatings. These particles may ultimately end up in the aquatic environment where they can be taken up by a variety of species, from both water and sediment. Yet, a mechanistic understanding of the bioaccumulation of these particles, especially from sediment, is lacking. Here we characterize the bioaccumulation kinetics of Ag after waterborne and dietborne exposures to Ag ENPs in the sediment dwelling oligochaete, *Tubifex tubifex*. Specifically we exposed worms to a range of environmentally realistic Ag concentrations: Ag was added as Ag ENPs or AgNO₃. Worms were exposed in OECD water (ISO 6341-1892) for 4h to estimate unidirectional uptake rate constants from water, or in sediment amended with Ag ENPs or AgNO₃ to determine Ag assimilation efficiency from food, a proxy for bioavailability. Ag elimination (both forms of Ag and both exposure routes) from worm tissues was characterized after transferring pre-exposed worms to clean media (OECD water) for up to 20 days. Results show that *T. tubifex* efficiently assimilated AgNO₃ from solution with an uptake rate constant of 8.2 L g⁻¹ d⁻¹. After 48h exposure to waterborne AgNO₃ followed by up to 20 days in clean conditions, no significant loss of Ag was detected ($p=0.57$). Sediment exposures to Ag ENPs showed uptake and partial elimination of Ag. Thus, large Ag body concentrations are expected in *T. tubifex* after exposure to both Ag forms, which might impact higher trophic levels in freshwater ecosystems, as *T. tubifex* is natural prey to many organisms.

Monday, August 15, 2016
Poster Session I
R-107

NANOGRA : a NANO Global Risk Assessment Project

Matthieu Hemart, ISSeP
TiÃ©coura Sinaba, Elodie Bouhoulle, HervÃ© Breulet, ISSeP

The increasing use of nanoparticles for materials and products more and more numerous and varied raises questions about the risks they may present for both the public and industries that use them. As such, nanotechnologies and their products represent a serious challenge to the authorities responsible for environmental policies and human safety. The NANOGRA project proposes a problematic global approach to nanoparticles risks by a multidisciplinary assessment based on different fields of study. The impact of nano-sized particles on the risk of explosion and/or inflammation in companies that use and/or store these substances will be studied according to the following parameters of interest: the ignition by determining the minimum ignition energy, the minimum ignition temperature and the minimum explosible concentration, the explosion by determining the maximum pressure, the maximum speed of pressure rise and the Kst constant checked for microscopic substances. The toxicological risks for exposed workers in these businesses and consumers through the use of certain product lines will be evaluated using several graded risk management tools ("control banding"), usually involving a double entry matrix, which combines a quantitative assessment of the dangerousness of nanomaterials with the likelihood of exposure by inhalation. A comparative study of the various management tools will be conducted on selected nanoparticles for explosion/flammability and ecotoxicological components. The potential impacts to ecosystems associated with a certain dispersion of nanoparticles in environmental media will first be assessed by laboratory experiments before extrapolating to field experiments. In the case of an accidental release of nanoparticles in the environment in Belgium, sediments will likely be the final medium of the released nanoparticles (leaching of dust for ex). Sediment organisms will probably be the most affected by this new kind of contaminants. A first laboratory approach on artificial sediment spiked with nanoparticles should assess the lethal and sublethal risk for *Chironomus riparius* and *Heterocypris incongruens*. The nanoparticles were selected on the basis of different nanoparticles emission sources identified in Wallonia and/or industrial strategic directions. The experimental protocols for each part of the project, the choice of nanoparticles and the first results will be available discussed here.

Monday, August 15, 2016
Poster Session I
R-108

Fate and effects of engineered silver nanoparticles in the aquatic-terrestrial transition zone: A floodplain mesocosm study

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Understanding the relation between fate and biological effects of engineered nanoparticles (ENPs) in environmental systems requires the transfer of state-of-the-art lab-scale knowledge to real-world situations as a first step toward natural systems. In this study we present a newly developed floodplain mesocosm system, which enables the characterization of fate, distribution, transport and effects of ENPs in the aquatic-terrestrial transition zone. The mesocosm system links aquatic and terrestrial aging of ENPs in one system under consideration of flooding dynamics. Using this system we evaluated the environmental fate and biological effects of silver nanoparticles (Ag NPs) close to concentrations as predicted for surface waters. The mesocosm system was run with natural water from the River Rhine, natural repacked soil from a Rhine floodplain and quartz sand as sediment phase. The flooding events were simulated every 3 weeks lasting for 4 days. After a pre-equilibration phase of 2 months, the mesocosm system was run with a pulse input of Ag NPs (pulse duration: 3 weeks, interval between pulses: 3 weeks). The impact of Ag NPs on the benthic organisms was investigated in the bioassays with *Gammarus fossarum* during and between the

Ag NP pulses. The total duration of the experiment was 33 weeks. The results of the experiment showed fluctuating but successively increasing concentrations of silver in the aqueous phase. Only 3 - 12% of the silver detected in the aqueous phase was dissolved. High contents of silver were found in the top layers of the soil and sediment. However, the feeding activity of *Gammarus* was not consistently affected. The absence of the toxic effects is most likely due to the low concentrations of silver applied in the experiment and low amount of dissolved silver. Extremely high enrichment factors (up to 30000) of silver were determined for algae. At the end of the experiment 0.5% of the silver was still in the aqueous phase and the remaining fraction was distributed between algae, soil and sediment. Consequently, large part of the Ag NPs detected in top layers of the soil and sediment may serve as a continuous source of toxic silver ions or may be remobilized again. Furthermore, the high accumulation of silver in algae suggests the enrichment of silver in aquatic organisms feeding on algae as a reasonable scenario.

Monday, August 15, 2016
Poster Session I
R-109

Environmental fate of a nano-insecticide and consequences for environmental exposure assessment

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The development of nano-enabled agrochemicals has recently received a lot of attention. Agrochemicals are intentionally applied in the open environment and the use of the new nano-products could thus result in relatively large amounts of engineered nanoparticles released (including directly on food crops). The adequate exposure assessment of nano-enabled agrochemicals is essential to identify the potential new risks and benefits that the new products represent, relative to currently used agrochemicals. There is however very little data on the environmental fate of the nano-enabled agrochemicals, and it is not known whether they can be adequately evaluated within current regulatory framework. The present study considered a series of insecticide nanoformulations and aimed at evaluating (i) the extent to which a nanoformulation may affect the fate of the insecticide in soil, and (ii) how discrepancies could be integrated in fate modelling for environmental exposure assessment. Sorption and degradation parameters of the insecticide were measured for (i) the pure active ingredient, (ii) a series of nanoformulations, and (iii) a commercially available formulation. In most cases, fate parameters derived for the nanopesticides were significantly different to those derived for the pure active ingredient (which currently serves as a base for a large part of the environmental risk assessment). Techniques developed for inorganic nanoparticles only provided limited (and sometimes misleading) information when applied to the organic nanoparticles present in the nanoformulations studied. More work will thus be necessary to design adequate analytical strategies to detect and characterize organic nanoparticles in environmental matrices. Finally, experimental fate parameters were used to carry out a series of exposure modelling exercises. Predicted environmental concentration very much depended on the modelling approach adopted to account for the impact of formulations on fate parameters. Overall, this study represents the first step towards the development of suitable approaches to evaluate the fate of organic nanoparticles in the environment. Such approaches are urgently needed to support the design of more intelligent nano-enabled delivery systems for pesticides and other bioactive substances, while ensuring their robust assessment by regulators.

Monday, August 15, 2016
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R-110

Use of nZVI and bimetallics Nps Fe/Cu in the removal of As present in aqueous matrices

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The use of Fe⁰ nanoparticles (nZVI) has presented a great interest like adsorbent material. This nanomaterial is widely used for the removal of organic and inorganic pollutants present in aqueous matrices¹. Similarly, the use of Fe/Cu bimetallic nanoparticles (Bi-Fe/Cu) with better performance than nZVI, have had an increase in the last years. The bimetallic nanoparticles present a higher reactivity, colloidal stability and removal rate compared with nZVI². The aim of this work was to synthesize and characterize nZVI and Fe/Cu bimetallic nanomaterial, evaluating the effect of Cu in the removal of As V present in aqueous matrices. The synthesis of nanomaterials was performed following the experimental procedure proposed by Wang & Zhang (1997). The change to the proposed synthesis was performed considering the simultaneous reduction of both metals, using NaBH₄ as a reducing agent. SEM images showed the formation of characteristic agglomerate of this magnetic material (nZVI). For the cases of bimetallic nanoparticles, the formation of branches (chains) of greater length was observed. Similarly, it was possible to determine the approximate particle size, for nZVI (82 nm), B1 (64.0 nm) and Bi-Fe/Cu (53.4 nm). The sorption Isotherm were carried out in batch system, working with 50 mg of nanomaterial and a solution of 200 mg/L As V (As₂O₅), 0.01 M NaCl (background electrolyte), pH 7, and stirred time of 5 hours. This study showed that the Freundlich Model presented a better mathematical fits, insinuating that there is a heterogeneous surface and multilayer sorption. The Bi-Fe/Cu are those with a major removal capacity (50.05 mg/g). In base on studies, the cooper (Cu) in Bi-Fe/Cu, considerably improves the removal capacity. This material can be applied as an absorbent nanomaterial for the arsenate abatement.

Monday, August 15, 2016
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R-111

Using molecular probes to investigate the interactions of substituted aromatic hydrocarbons with fullerenes

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The understanding and prediction of molecular interactions between organic compounds and carbon-based nanomaterials is crucial to interpret their phase transfer processes in environmental matrices. In addition, such knowledge would be beneficial to assess the potential application of these materials as special sorbents, e.g., for sample preparation. While there is a lot of sorption data for carbon nanotubes, little information is available on the interactions between organic compounds with C60 fullerenes. In a previous study we have investigated the effect of UV-induced surface oxidation on the sorption behavior of C60 [1]. Changes in surface chemistry led to significant alteration of both sorption affinity and capacity. The results indicated that in addition to non-specific van-der Waals and electron donor-acceptor-interactions, the presence of oxygen-containing functional groups on the C60 surface potentially allowed for the contribution of hydrogen-bond interactions. However, sorption data for a much broader compound set using molecular probes with various functionalities are necessary to further investigate the contribution of individual interactions to overall sorption.

To systematically study this process, the combined effects of -OH/NH₂ functional groups of aromatic organic compounds and surface oxygen-containing functional groups on C60 on the interactions were evaluated. We combined two multi-phase sorption batch experiment approaches using a passive sampling technique applying polyoxymethylene and a headspace in-tube microextraction. This approach allows for a systematic comparison of the interactions between C60 and organic compounds with significantly different physico-chemical properties (e.g., aromaticity, functional groups, etc.).

Monday, August 15, 2016
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R-112

Effects of most common engineered nanoparticles on the biogas production at waste water treatment plants

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Engineered nanoparticles (NPs) continue to be exponentially used in numerous products, with the consequence to be released into waste water treatment plants (WWTP). Between the most produced NPs we find TiO₂, ZnO and Ag, being the ones with more probability to attain WWTP (1). Approximately 85 % of those NPs will end up in the sludge (2), with the most probable effects happening on the anaerobic digestion part, where biogas is produced. These possible effects can be established by following the methane yield.

In this study, the methane yield is being investigated after short-term exposure of the sludge to the above-mentioned NPs in digestion batch tests. The injected sludge and regular activated sludge were both conditioned with a synthetic substrate to keep the digestion conditions invariable. Different phases (total phase and soluble phase) of the sludge during the biogas production were observed in order to localize more precisely the occurring effects. The total phase contain sludge flocs, which can easily adsorb NPs, affecting their fate, whereas the soluble phase (filtered through <0.8 mm pore size) contains much smaller colloids but also with the capacity to adsorb the NPs. NPs aggregation state before injection was characterized by NanoSight NS500.

Data obtained until now surprisingly shows 17 % more pronounced effects on the dynamic of methane production in the soluble phase than in the total phase. Furthermore a time-dependent retention has been observed in the soluble phase. Evidently, this is of high importance on the dynamic of methane production over time, since the several bacteria responsible for specific parts of the methane production process have different time activities. In addition, the amount of methane yield is determined by different NPs. ZnO injected sludge shows the most increase by about 5%.

EFFECT OF NANO-ZEOLITE AND BIOSOLIDS ON PLANTS GROWN IN SALINE SOILS

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Soil salinity poses a significant threat to agricultural productivity worldwide as it impacts plant growth and yield. Three hectares of cultivated land is lost every minute due to salinization through anthropogenic activities and one third of irrigated land is already degraded by salinity (Ghassemi et al., 1995). High concentrations of salts create ion toxicity and nutrient imbalances which disrupt plant growth and development, as sodic soil is usually low in organic matter (Naidu and Rengasamy, 1993; Silberbush and Ben-Asher, 2001). Like other organic materials, biosolids which are rich in organic matter and essential plant nutrients are often used as soil amendments although they are also a potential source of trace elements that, if transferred to humans, may cause adverse health effects. Soil salinity usually increases the bioavailability of heavy metals in soils treated with biosolids. Zeolites are microporous aluminosilicate minerals that are used as an amendment for the remediation of contaminated soil. Mineral zeolite has ability to release nutrients slowly and enhance plant growth. However, it is important to determine the effect of soils treated with nano-zeolite and biosolids together on plant growth and metal accumulation under salt stress. In this study we investigate the effect of nano-zeolite in combination with biosolids as a sodic soil amendment on plant growth and metal accumulation.

METHODS

In this pot experiment, soil was collected from an agricultural site, Virginia, South Australia, in which particle size distribution was 71% sand, 13% silt and 16% clay and the taxonomic classification was loamy. The soil and biosolids were oven dried and passed through a 2-mm sieve and analyzed for pH (8.52 and 7.6), EC (0.4 and 8.21 MS/cm), TOC (41 and 806 ppm), Cl⁻ (60 and 8218 ppm), NO₃ (498 and 12094 ppm), SO₄ (24 and 12930 ppm) and PO⁻³ (17 and 264 ppm) in water and CEC (134 and 412 ppm) in NH₄Cl, Na (109 and 1206 ppm), K (530 and 1170 ppm), Ca (9224 and 14088 ppm) in aquia regia, respectively. The soil was spiked with Na solution as chloride salt for preparing four different Na levels - 0, 20, 40 and 60 dS/m - and biosolids were mixed at a rate of 20% on w/w basis, while 1% zeolite Na type A (Na₂O.Al₂O₃.2SiO₂.4.5H₂O) was added according to treatments. The sixteen treatments were i. control soil, ii. salinity 2.0 dS/m, iii. salinity 4.0 dS/m, iv. salinity 6.0 dS/m, v. soil + zeolite 1%, vi. salinity 2.0 dS/m + zeolite 1%, vii. salinity 4.0 dS/m + zeolite 1%, viii. salinity 6.0 dS/m + zeolite 1%, ix. soil 80% + biosolids 20%, x. soil 80% + biosolids 20% + salinity 2.0 dS/m, xi. soil 80% + biosolids 20% +

salinity 4.0 dS/m, xii. soil 80% + biosolids 20% + salinity 6.0 dS/m, xiii. soil 80% + biosolids 20% + zeolite 1%, xiv. soil 80% + biosolids 20% + salinity 2.0 dS/m + zeolite 1%, xv. soil 80% + biosolids 20% + salinity 4.0 dS/m added + zeolite 1%, xvi. soil 80% + biosolids 20% + salinity 6.0 dS/m + zeolite 1%. The experiment was laid out in a randomized block design and replicated four times. Lettuce seeds were sown in the treated soil and Hoagland solution was used as a nutrients source and applied as needed. The plants were harvested after 8 weeks. The harvested lettuce shoots were analysed after oven drying and then digested with concentrated nitric acid. Their metal content was then measured by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Compared to the control, the different levels of Na alone and the combination of Na and zeolite 1% led to reduced lettuce shoot dry weight, while no plant grew at the highest level of Na (60 dS/m) stress. The biosolids amended soil (20% w/w) resulted in increased shoot dry weight under all Na stress levels. The combined use of zeolite with biosolids did not show any significant differences of shoot dry weight at control and 20 dS/m but displayed significant variation at 40 and 60 dS/m of Na levels (Fig. 1b). These results are consistent with the plant height (Fig. 1a) and shoot Na and K content (Fig. 1c and 1d) because higher cellular Na and lower K inhibit the growth of lettuce. This suggests that zeolite Na type A could not overcome salinity-induced growth inhibition and Na uptake into plants grown in contaminated soil.

CONCLUSION

Biosolids can be used as effective amendment in sodic soils to mitigate salt stress. However the addition of synthetic zeolite Na type A was found not to enhance plant growth and K uptake under salt stress.

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Towards test guidelines for predicting fate and bioavailability of CuO- and ZnO-enabled agrochemicals

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There are a number of agrochemicals using metal and metal oxide nanoparticles as antifungal agents. There is a need for understanding how the particle and soil properties affect their fate and bioavailability in agricultural soil. The objectives of this research were to determine if existing testing guidelines for assessing metal bioavailability in soils are also usable for nanoparticulate forms of those metals. We measured the extractability of Cu in standard soils dosed with either CuO-NPs or Cu(NO₃)₂ using two commonly used extraction methods for assessing bioavailability: 0.01M CaCl₂ and 0.005M DTPA (pH 7.6). We performed these extractions at selected time points to determine how aging of the ions or particles affects their extractability. We also monitored changes in the speciation of Cu in soil using X-ray absorption spectroscopy. For soils dosed with 100 mg Cu Kg⁻¹ dried soil CuO-NPs or Cu(NO₃)₂, there was marked differences in the amount of extractable Cu. At the maximum, CuO NPs was ~50% less extractable than the Cu from Cu(NO₃)₂. The temporal trends for DTPA- and CaCl₂-extractable Cu from CuO-NP amended soil were very different than for Cu(NO₃)₂-amended soil. For CuO NPs, extractability increased with time from a 3wt% after a day to 30wt% after 31 days. For Cu(NO₃)₂ amended soils, Cu availability decreased over time from ~80wt% after 1 day, to ~65 wt% after 31 days. The increase in extractability of CuO-NPs in soil with time was due to its slow dissolution of, as inferred from changes of speciation from CuO to Cu-Humic acid observed by X-ray absorption near edge structure. Our findings suggest that dissolution and aging are the key factors controlling CuO-NPs' bioavailability in soil, and suggest that test guidelines to predict bioavailability will need to consider time as a test variable.

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R-115

Ingestion, bioaccumulation, and depuration of titanium dioxide nanoparticles by the blue mussel (*Mytilus edulis*) and the eastern oyster (*Crassostrea virginica*)

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Sedentary organisms such as suspension-feeding bivalves are particularly vulnerable to anthropogenic contaminants, such as nanoparticles, that enter coastal environments. The purpose of this work was to examine the ingestion, bioaccumulation, and depuration rates of TiO₂ nanoparticles by two species of suspension-feeding bivalves, the blue mussel (*Mytilus edulis*) and the eastern oyster (*Crassostrea virginica*). Two representative TiO₂ nanoparticles, UV-Titan M212 (Titan) and Aeroxide P25 (P25), were delivered to the animals either incorporated into marine snow or added directly to seawater at a concentration of 1.0 mg/L for exposure periods of 2 and 6 hours. After feeding, the animals were transferred to filtered-seawater and allowed to depurate. Feces and tissues were collected at 0, 12, 24, 72, and 120 hours, post-exposure, and analyzed for concentrations of titanium by inductively coupled plasma-mass spectrometry. Results indicated that the capture and ingestion (i.e., transfer to the gut) of TiO₂ nanoparticles by both mussels and oysters was not dependent on the presence of marine snow, and weight-standardized clearance rates of bivalves exposed to TiO₂ nanoparticles were not significantly different than those of unexposed control animals. Both species ingested about half of the nanoparticles to which they were exposed, and > 90% of the nanoparticles were egested in feces within 12 hours, post-exposure. Findings of this study demonstrate that mussels and oysters can readily ingest both Titan and P25 nanoparticles regardless of the form in which they are encountered, but depurate these materials over a short period of time. Importantly, bioaccumulation of Titan and P25 nanoparticles does not occur in mussels and oysters following exposures of up to 6 hours.

Monday, August 15, 2016
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R-116

Nanosafety of nanozinc fertilizer and mesoporous silica nanocarrier in vitro

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Nanomaterials safety is a major challenge and is a considerable hindrance against the full use of nanotechnology and its products. Nanofertilizer and nanocarrier/ semiochemical carrier are the products of nanotechnology which are used to enhance the production and to deliver a variety of compounds including drug, pesticide & fertilizer release, respectively. Micronutrients mainly in their nano-sized form are applied as a nanofertilizer while mesoporous silica is profoundly used as a nanocarrier. The environment and humans are directly exposed to them from workplace/production area, during their particular application or through food chain. Once released, there is no mechanism to recall these nanomaterials. Their fate in the environment and health ramifications for humans, animals and other life forms is still mystery. It is therefore imperative to develop models to predict the fate and eco-safety of nanomaterials employed in their production, generate comprehensive nanosafety data of these nanomaterials, to establish safety standards for workers and most importantly develop nanotechnologies in food and agriculture that employ safe nanomaterials. Hence, under present study, impact of in vitro treatment with different concentration of nano-zinc fertilizer (NZF) and mesoporous silica nanocarrier (MSN) on immune cell as well as germ cell in terms of cytotoxicity test (MTT: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, NR: Neutral red assay) along with the measurement of major oxidative stress enzymes (SOD: Superoxide dismutase, GPX: Glutathione peroxidase) were carried out. In vitro treatment of neutrophils and germ cell above 50- $\mu\text{g}/\text{ml}$ of NZF resulted in a significant ($p < 0.01$) decrease in 50% or more percentage viability (%viability) as compared to control as depicted by MTT and NR assay. Likewise, a significant ($p < 0.05$) decrease in SOD and GPX activity were observed in both cases. But in case of cells treated with MSN there was no significant changes in %viability as well as in the activities of oxidative stress enzymes even at higher concentrations. These results suggest that nanozinc fertilizer is toxic to the cell when applied at incrementally higher concentrations whereas mesoporous silica nanocarrier is safe even at such higher concentrations.

Tuesday, August 16, 2016
Poster Session II
R-201

Environmental fate and transport of titanium dioxide nanoparticles in municipal wastewater effluent in outdoor stream mesocosms

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Titanium dioxide (TiO₂) nanomaterials are ever more widely used for many applications and across many industries. As their production and use continues to increase so does the risk of release into aquatic environments. However, risk assessments for engineered nanomaterials have been challenging. While there is a growing body of research on the toxicity of TiO₂ nanoparticles (NPs), risk assessments must also account for TiO₂ NP behavior, fate and transport, and bioavailability at environmentally relevant concentrations in complex ecosystems. Here, we present fate and transport results of a 35-day stream mesocosm study. TiO₂ NPs were added continuously for 28 days into 20 m long artificial streams running partially recirculating municipal wastewater effluent to reach nominal TiO₂ concentrations of either 5 mg L⁻¹ (high) or 50 µg L⁻¹ (low), in addition to control streams with only effluent. Results from ICP-MS analyses for Ti concentrations in water indicate that the low streams remained similar to the controls, ranging from 1-8 µg L⁻¹, indicating that the low concentration was environmentally relevant, especially for effluent-dominated waters. On the other hand, the high streams had concentrations that remained relatively stable throughout the dosing period at 100-300 µg L⁻¹. There was up to an 80% decrease of Ti in the water column 1 day after cessation of dosing in both the low and high streams, followed by a less dramatic steady decrease in the final week of the study. Periphyton concentrations in control and the low streams similarly did not differentiate from each other, with concentrations of 100-600 mg Ti kg⁻¹ dry weight, with no observed accumulation or increase in Ti concentration throughout the 28 day exposure period. However, periphyton Ti concentrations in high streams increased throughout the first 28 days, reaching concentrations of 2,500-10,800 mg Ti kg⁻¹ dry weight. A 40% decrease in Ti concentration was observed at day 35, 7 days after cessation of Ti treatment. The riffle, run and pool habitat types had differing concentrations of Ti in periphyton as a result of location relative to the dosing site and/or flow conditions and water depth. Periphyton in the run section with fish grazing activity had lower concentrations of Ti than in the ungrazed sections, indicating that both stream region and level of disturbance influenced Ti concentrations in periphyton.

Tuesday, August 16, 2016
Poster Session II
R-202

Nanosilver Conductive Ink: A Case Study for Evaluating the Potential Risk of Nanotechnology under Hypothetical Use Scenarios

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Engineered nanomaterials (ENMs) are being incorporated into a variety of consumer products due to unique properties that offer a variety of advantages over bulk materials. Understanding of the nano-specific risk associated with nano-enabled technologies, however, continues to lag behind research and development, registration with regulators, and commercialization. One example of a nano-enabled technology is nanosilver ink, which can be used in commercial ink-jet printers for the development of low-cost printable electronics. This investigation utilizes a tiered EHS framework to evaluate the potential nano-specific release, exposure and hazard associated with typical use of both nanosilver ink and printed circuits. The framework guides determination of the potential for ENM release from both forms of the technology in simulated use scenarios, including spilling of the ink, aqueous release (washing) from the circuits and UV light exposure. The as-supplied ink merits nano-specific consideration based on the presence of nanoparticles and their persistence in environmentally-relevant media. The material released from the printed circuits upon aqueous exposure was characterized by a number of analysis techniques, including ultracentrifugation and single particle ICP-MS, and the results suggest that a vast majority of the material is ionic in nature and nano-specific regulatory scrutiny may be less relevant.

Tuesday, August 16, 2016
Poster Session II
R-203

Degradation and Release of Nanoparticles used for UV Protection on Outdoor Surfaces

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With the continued inclusion of engineered nanoparticles (NPs) in consumer products, a detailed understating their release during use is critical in determining their potential effect on human and environmental health. Of particular interests are commercially available NP-based surface coatings including paints, stains, and sealants as they represent an area of direct contact between the product, the consumer, and the surrounding environment. In this study thoroughly characterized cerium oxide and zinc oxide NPs, marketed as additives to paints and stains for their increased UV protective properties, were dispersed in either Super-Q Water, or a commercially available deck stain. NP dispersions were applied to either Micronized-Copper Pressure treated Lumber or a composite decking material. The potential for the NP release from these coated surfaces was evaluated by leaching the coated samples in Synthetic Precipitation Leaching Procedure Solution (pH 4.2) for 72 hours. The total concentrations of cerium and zinc released was tracked through ICP-OES, while the speciation (ionic versus particulate) was determined through sequential filtration and X-Ray Absorption Fine Structure Spectroscopy. The results indicate that both the dispersion solution (water versus stain) has a major effect on the extent and form material released from the surface. Critically, these results demonstrate the transformation and release of pristine NPs and related degradation products during the consumer use phase.

Tuesday, August 16, 2016
Poster Session II
R-204

The Efficacy of A Nano-TiO₂ Enabled Floor Coating and Its Environmental Implications

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Until recently, the analysis of the efficacy and unintended consequences (i.e., hazard and exposure) of engineered nanomaterials (ENM) has been almost exclusively focused on pristine nanomaterials. To fully understand the potential impacts and risks of nanomaterials from a life cycle perspective, further investigation is required not only on the nano-enabled products but also on the release and transformation of ENMs during use and disposal. This presentation examines both the benefits and impacts of a floor coating product containing nano-TiO₂. To simulate the release scenario from daily use, a Taber abraser is employed to elucidate the influence of various parameters on the release of nano-TiO₂, such as type of support, abrasive materials, and weight stress. The desirable characteristics (i.e., efficacy) of scratch resistance and antimicrobial activity are examined on various support materials after abrasion, and are compared against the non-worn coating. The released particles are also collected and characterized by electron microscopy for size distribution and exposure potential of TiO₂ nanoparticles (as individual ENMs and embedded in polymer). The released particles from coating are further examined for their photocatalytic reactivity with respect to reactive oxygen species formation, as a potential indicator for environment impacts on rivers that may become a sink for worn ENM-polymer materials. This presentation offers a case study in demonstrating the efficacy of a consumer product containing ENM, which can be extended to other product lines to predict the environmental implications of ENM and to improve design of safe nano-enabled products.

Tuesday, August 16, 2016
Poster Session II
R-205

Multi-day diurnal measurements of nanoparticle and organic chemical release from sunscreen use in natural surface water

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Clear Creek in Golden, Colorado sees a large number of recreational users during summer, which is expected to result in release of sunscreen chemicals to the water. In this study, water samples were collected hourly for 72 hours over a busy holiday weekend, and were analyzed for the organic chemical - based (oxybenzone) and inorganic colloidal (titanium dioxide) active sunscreen constituents. An increase in oxybenzone concentration was observed daily during each day's peak recreational use, approximately 12:00 to 19:00 hr. This corresponded with an increase in titanium concentration. Metals naturally co-occurring with titanium such as aluminum and iron also showed an increase of these elements during bathing periods as well, suggesting the titanium increase may also be partially the result of sediment resuspension. The ratio of titanium to both aluminum and iron increases relative to the background elemental ratios during peak recreational use, suggesting an anthropogenic source of titanium. Single particle ICP-MS (spICP-MS) was used to analyze water samples for Ti-containing particles. Overall, this is the first consecutive-multi-day monitoring study for NPs released from sunscreen to a natural water system, and it highlights the challenges in dealing with detection of NPs above a natural background.

Tuesday, August 16, 2016
Poster Session II
R-206

Effect of short term exposure of ZnO and TiO₂ nanoparticles on algae: *Chlorella pyrenoidosa* & crustacean: *Daphnia* sp.

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Zinc oxide (ZnO) and Titanium dioxide (TiO₂) nanoparticles are some of the widely used nanoparticles (NPS) in commercial industry. Thus the chances for the particles to get run off to the aquatic environment and to there by affect the aquatic life are high. The present study evaluates the short term toxicity of ZnO NPs and TiO₂ NPs on *Chlorella pyrenoidosa*, which is a fresh water algae and on *Daphnia* sp. which is a common crustacean found in fresh water bodies. NPs were synthesized via chemical co precipitation technique and characterized UV-visible spectroscopy, X Ray Diffraction, XPS, Transmission Electron Microscope, Scanning Electron Microscope, Zeta sizer and Zeta potential analyzer. . The dosage of the particles was from 0.001 mg/L to 100 mg/L. The study evaluated the chlorophyll content, lipid peroxidation, intra cellular protein and extra cellular protein as a measure of toxicity for *C. pyrenoidosa*. The study found that the algae produced excessive amount of extracellular polysaccharides when it gets interacted with the NPs. The light microscopic evaluation also found the agglomeration of algal cells when interacted with NPS. The mortality of *Daphnia* sp. was also studied both in the dark condition and also after the irradiation of sunlight. The interacted organisms were observed under phase contrast microscope and the images were taken.

Tuesday, August 16, 2016
Poster Session II
R-207

Surface Characterization of Nanoparticulates from Solid Biomass Combustion and the Impact of Natural Organic Matter

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As the use of biomass as a renewable fuel source is encouraged owing to either increasing fossil fuel prices or incentive programs, the implication of its effect on ambient air quality must be fully understood. In this proposal experiments using harvested wood combustion emission nanoparticles from various boilers, both advanced and conventional, with various biomass fuel types will be characterized to provide new insights about the interactions of biomass combustion nanoparticulates (and their aggregates) with natural organic matter (NOM). The proposed reach will also examine nanoparticles from different phases of burn cycle (start-up, steady state, modulated loads, and burn-out). Specifically this proposed work will focus on surface analysis methods for detailed characterization of combustion produced nanoparticles along with the impact that shape, reactivity and environmentally induced changes have on the nanoparticulate properties. The results from the study are planned to provide data for manufacturing and policy decision making for safer, efficient use of wood-fired heating devices.

Agro waste as precursor for synthesis of iron-oxide nanoparticles and its effect on growth performance, muscle composition and digestive enzyme activities of the freshwater prawn *Macrobrachium malcolmsonii*

Asaikkutti Annamalai, Bharathiar University

The green bio synthesized Fe₂O₃ nanoparticle (iron-oxide NPs) using *Vitis vinifera* peel extract was characterized by various techniques. HR-SEM photograph showed that iron oxide NPs (Fe₂O₃ NPs) were spherical in shape, particle size was 50-80 nm. The Zeta potential revealed the surface charge of Fe₂O₃ NPs obtained from *V. vinifera* extract is around 33.28 mV. Further, the iron oxide NPs was dietary supplemented for freshwater prawn *Macrobrachium malcolmsonii*. Fe₂O₃ NPs were supplementary to the experimental basal diets at the rates of 0 (control), 0.5, 1, 2, 4, 8, and 16 mg/kg dry feed weight. *M. malcolmsonii* were fed these Fe₂O₃ NPs supplemented diets for the period of 90 days. Here the present findings illustrated that prawns fed with 0.5-8.0 mg/kg Fe₂O₃ NPs supplemented diets achieved significant ($P < 0.05$) enhancement in survival rate, growth performance, digestive enzyme activities, and muscle biochemical compositions. Though, the prawns fed with 16 mg/kg of nano-Fe showed better performance. The antioxidants enzymatic activity, metabolic enzymes status in muscle and hepatopancreas showed no significant ($P > 0.05$) alterations in prawns fed with 0.5-8.0 mg/kg Fe₂O₃ NPs supplemented diets. However, the prawns fed with 16 mg/kg Fe₂O₃ NPs showed meager performance. Hence, the present work suggests that 8.0 mg/kg Fe₂O₃ NPs can be supplemented for regulating enhanced survival, growth and production of *M. malcolmsonii*. Consequently, the data of the present study proposed addition 8.0 mg/kg Fe₂O₃ NPs diet to progress prawn growth and antioxidant defense system.

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Poster Session II
R-209

Synergistic Effect of Chemo and Photothermal for Breast Cancer Therapy Using Polyethylene Glycol (PEG) Coated Zinc Oxide Nanoparticles

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Modern therapy of malignant breast cancer in clinic is unsatisfactory with deprived patient compliance due to stumpy therapeutic efficiency and strong systemic side effects. Herein, we combined chemo-photothermal targeted therapy of breast within one novel multifunctional drug delivery system. Polyethylene glycol (PEG) coated Zinc Oxide nanosheet (PEG-ZnO NS) was successfully synthesized and characterized, and first introduced to the drug delivery field. A doxorubicin (DOX)-loaded PEG-ZnO NS based system (DOX-PEG-ZnO NS) showed heat stimulative, pH-responsive, and sustained release properties. Cytotoxicity experiments demonstrated that combined therapy mediated the highest rate of death of breast cancer cells compared to that of single chemotherapy or photothermal therapy. These findings provided an excellent drug delivery system for combined therapy of breast due to the advanced chemo-photothermal synergistic targeted therapy and good drug release properties of DOX-PEG-ZnO NS, which could effectively avoid frequent and invasive dosing and progress patient compliance. In vivo toxicity evaluation showed that DOX-PEG-ZnO NS contain squat systemic toxicity in murine model system. Cancer cell specific targeted delivery (TDD) by sheet nanocarrier is on a high role. The present investigations prove that the DOX-PEG-ZnO NS has low toxicity and enhance therapy efficacy, which endow with credible supports for the biosynthesized DOX-PEG-ZnO NS as a vital candidate for a drug delivery system.

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R-210

Oxidation of green rust to nano crystalline $MFeO_2$ and $M_xFe_{3-x}O_4$ in aqueous solution. Nanoparticle synthesis to remove heavy metals (M) from wastewater

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Soraya Heuss-AÄ bichler

Engineered nanoparticles are discussed to constitute a risk to the environment. We present here a new method to produce nanoparticles with the target to avoid the release of heavy metals into the environment. Heavy metal pollution has become one of the most serious environmental problems today. In various industrial branches wastewater with partially high concentrations of metallic components are produced. Though there are various techniques to treat wastewater, especially in developing countries heavy metal containing wastewater is discharged without treatment into the environment. These wastewaters are hazardous to the environment and pose potential health risks for humans and ecosystems. After the commonly used treatment method only small fractions of the lime-hydroxide sludge are recycled, due to the high water and low heavy metal content. We developed a facile, environmentally friendly and economic method to remove heavy metals from wastewaters at low temperatures (40 °C - 90 °C). At the same time we synthesize zero-valent phases, oxides as delafossite ($AFeO_2$), ferrite ($M_xFe_{3-x}O_4$), doped heavy metal oxides (MO and M_2O). All precipitates are exclusively nanoparticle in size. We are able to replace energy-intensive synthesis methods, e.g. via high temperature solid state reactions, sol-gel methods with high temperature after treatment and under hydrothermal conditions. To characterize the nano-sized crystalline powders, different analytical methods, such as AAS, ICP-OES, XRD, FTIR, SEM, TEM, MÄ¶Ä bauer and magnetic measurements (VFTB and PPMS), are combined. Green rust GR [$Fe_2+4Fe_3+2(OH)_{12} * SO_4$] precipitates first. Our results show, that the oxidation of GR is a key step in the wastewater treatment process and mainly controls the later synthesis product. The final phase assemblage depends strongly on the reaction and ageing parameters, e.g. Fe-addition, reaction temperature, kind of metal, initial concentration of heavy metals, pH value, alkalization and ageing temperature and time. Oxidation products of GR are ferrite, ferrihydrite ($Fe_{10}O_{14}(OH)_2$), or sometimes goethite ($\pm FeOOH$). Novel is the formation of delafossite as possible oxidation product of GR. Our results show that the specific heavy metal (M) present in the solution strongly influences the transformation of GR to more stable phases during precipitation and subsequent ageing process. The wastewater treatment process is feasible for synthetic wastewater and industrial wastewater sample. At optimal conditions, the recovery rate of heavy metals is between 99.98 % and 100 % for Cu, Zn, Ni, Ag, Pb, Cr, and Mn.

Tuesday, August 16, 2016
Poster Session II
R-211

Stability of 2D MoO₃ in Biological and Environmental Media

Evan Gray, Brown University

Continuing evolution in nanotechnology research has identified new classes of two-dimensional nanomaterials (NMs). This wide range of materials has numerous applications including but not limited to electrodes in lithium ion batteries, lubricants and as antifouling agents. The production, use and subsequent disposal of these 2D materials raise questions regarding their overall fate and toxicity in human and environmental systems. This work focuses on 2D metal oxide materials, specifically MoO₃. Published solubility data for bulk 2D materials in water at neutral pH varies from insoluble up to 1.4 g L⁻¹ (MoO₃) at neutral pH. In more complex biological and environmental solutions, MoO₃ is predicted to dissolve through hydrolysis and reductive dissolution processes. If MoO₃ and other 2D oxide materials dissolve rapidly, any resulting risks will be those associated with exposure to the dissolved ion; however in cases of slower dissolution, exposure and uptake of the NM form could occur. This distinction between forms is important as dissolved ions and NMs have different uptake and toxicity mechanisms and understanding the fate of these materials is required to correctly assess toxicity and risk. Although the predicted solubility of MoO₃ is extremely high from a toxicological perspective, some biological conditions may slow dissolution to an extent where exposures to the NM form may be relevant. The stability of MoO₃ was assessed in two solutions: a phosphate buffered saline (PBS) that mimics the pH and ionic content of human body fluids and Dulbecco's Modified Eagle Medium (DMEM) a commonly used cell culture media. Ultraviolet visible spectroscopy (UV-Vis) scans indicated that NM MoO₃ dissolves in PBS from a starting concentration of 300 mg L⁻¹ in under 10 min. In DMEM however, complete dissolution at the same concentration is slowed to greater than 1 hour. Dynamic light scattering (DLS) measurements confirm dissolution by indicating a shift to smaller particle sizes over time in PBS solution and DMEM, though a larger change in size was observed in PBS. The slower dissolution of MoO₃ in DMEM implies that some biological fluids can stabilize these NMs and potentially create NM specific exposure scenarios. Continuing work will assess the stability of additional oxide NM including MnO₂, WO₃ and V₂O₅.

Tuesday, August 16, 2016
Poster Session II
R-212

Nanotechnologies' legal and social implications: the necessity of studying nano-materials products life cycle and its possible consequences to the health of workers and consumers.

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Raquel Von Hohendorff and Cristine P. Machado

The brilliant human mind has contributed to major technological advances such as nanotechnologies. Within these developments, complexed risks also arise, and acknowledging the possible risks to human health and the environment is important to maintain sustainable development in all stages of production, commercialization and waste. The first step to analyze in the life cycle of nano-products must be focused on the production of engineered nanoparticles, then address the manufacturing and waste management. Each step must be handled with responsibility, in order to evaluate the exposure of workers, consumers and the environment. This research combines the method functionalist with content analysis and textual review, in order to develop a interdisciplinary investigation. Bringing different fields together is beneficial to overcome the challenges brought by the nanotechnologies. As a result, distinct areas of expertise will open and close to one another, whereas they can mutually help each other comprehend the complexity of the reality brought by the advances of nano-scale, and also discuss the emerging necessity of nanotechnologies regulations. The legal system must observe the technological developments to assist finding more adequate regulatory frameworks. The best interdisciplinary science comes from the perception that there are always urgent questions that cannot be treated by researches of certain areas. When researching the term 'nanotechnology' in the scientific articles database of Web of Science published between 2010 and 2015, were found a total of 19.626 publications. Combining 'nanotechnology and risks' the sum drops to 1145 (5,83%). Searching for 'nanotechnology and environment risks' it was found 346 (1,76%) articles, and the terms 'nanotechnology and regulation' were found 443 (2,25%) articles. This data reveals that there is a lack of research focused on the possible risks of the nanotechnologies, as well as on its social and regulatory considerations. The development of nano-toxicology evaluation techniques and the analysis of products life's cycle are essential to enjoy the benefits with security and protection of the environment for present and future generations. The responsible advances of nanotechnology depends on reliable scientific capability to access and manage the risks, as well as decision making in governmental levels, seeking to consider the social impacts that this new technology may bring in the global sphere.

Tuesday, August 16, 2016
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R-213

Effects of particle surface charge on inhaled aerosolized mesoporous silica nanoparticles

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Particulate air pollution continues to be a serious air quality issue for the Central Valley of California. Particulate matter (PM) of all sizes arises from a wide range of sources. Of particular concern are ultrafine or nano-sized particles (particle less than 0.1 μm in diameter) which easily enter into the deep recesses of the lungs. We wish to investigate the influence of nanoparticle charge and its effects on deposition, uptake and translocation in the respiratory tract. Two sets of fluorescently-labeled 50 nm mesoporous silica nanoparticles (MSN), one with a positive surface charge and one with a negative surface charge, were aerosolized into aqueous droplets to model particulate matter. CD-1 male mice were exposed to either the positive or negative MSN aerosol for 5.5 hours. The mice were sacrificed immediately, 1 day, 7 days, or 21 days after the exposure. These timepoints allow for both acute and long-term effects of exposure to be analyzed. BALF (bronchoalveolar lavage fluid) will be analyzed for inflammatory responses and fluorescent observation of nanoparticle uptake. TEM will also be used to visualize the effects of charged particle uptake by macrophages in the BALF. Our most current results from this work will be presented.

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R-214

Detecting Single-walled Carbon Nanotube uptake by *Daphnia magna* Using single particle ICP-MS

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Unique physical and chemical properties of nanomaterials (NMs) lead to their numerous applications varying from fuel cell to drug delivery. The production scale of NMs expanded rapidly during the past few decades, raising concerns over their potential environmental impacts once released into the ecosystems. Though the amount of NMs released is very limited ($\mu\text{g/L}$ or lower) according to monitored and simulated results, the risk they cause still will be impressive. In the risk assessment of NMs, not only the ecotoxicity which NMs may bring, but also the chronic endpoints such as potential biological accumulation should be the interest. However, the study is still in infancy. For example, previous studies have tested the acute toxicity of carbon nanotube (CNT), as well as uptake and depuration by biological receptors. But CNT used in those studies were treated (lipid-coated or radioactive labeled), unlike CNT applied in industry and real life. In addition, the amount of CNT used in previous studies was much larger ($\mu\text{g/L}$) than predicted aqueous concentration (ng/L). In order to achieve more direct and reliable analysis of CNT, single particle inductively coupled plasma mass spectrometry (spICP-MS) is introduced. spICP-MS takes advantage of elemental analysis of ICP-MS which is capable to detect samples with ng/L concentration, but it is operated in a particle-by-particle basis allowing analysis of nanoparticles (NPs) shown as pulses. Usually used to detect metal NPs, spICP-MS is unable to detect CNT by carbon directly, but the residue metal NPs embedded in CNT structure due to catalytic synthesis can be used to monitor the presence and amount of CNT. Development of spICP-MS allows shortening dwell time from several millisecond to several microsecond, improves pulse resolution as well as suppresses background signals, providing better analysis both in mass and particle number. The optimized method, utilizing yttrium as the analyte, was applied to detect the uptake amount of CNT by *daphnia magna* after 48 hour exposure to a CNT suspension. Approximately 3% of the SWCNTs were absorbed by 10 *daphnia* adults, despite the original concentrations of the suspensions. Minimal toxicity was observed in this experiment using single-walled CNT with $400 \mu\text{g/L}$ and lower concentrations. Similar results were observed in experiments performed using CNT released from polymer nanocomposites.

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R-215

Stress-Induced Nanoparticle Release from Commercially Available Nanoceramic Cookware

Susana Addo Ntim, USFDA

Samuel Norris (NIST), Keana Scott (NIST), Lipiin Sung (NIST), Treye A. Thomas (CPSC) and Gregory O. Noonan (USFDA)

Food preparation and storage materials are often subjected to stressful conditions such as scraping and cleaning with abrasive pads throughout their lifecycle. Understanding the impact these conditions have on particle release is therefore important in assessing their safety. A nanoclay-enabled sauce pot and nanosilica-coated nonstick fry pan were evaluated for nanoparticle release after being subjected to linear abrasion with abrading attachments such as steel wool, stripping pads and a carbide burr to simulate stressful use. For the sauce pot, the migration profile of aluminum was not affected by the type of abrasion attachment used. Although the amount of aluminum migrating from the sauce pot increased after abrasion, nanoparticle release was not observed. For the nanosilica-coated fry pan, the type of abrasion attachment used produced a statistically significant difference in the silica migration profile. Abrasion with the carbide burr attachment damaged the fry pan beyond reasonable use producing detectable silica nanoparticle release.

cellulose nanocrystals supported nZVI nanoparticles with enhanced reactivity and mobility performance

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Zero-valent iron nanoparticles (nZVI) have been widely studied for in situ remediation of groundwater and other environmental matrices. nZVI are strongly reactive reducing agents capable of rapid degradation of chlorinated organic compounds, pesticides, organic dyes and are also effective in elimination of heavy metals and inorganic anions.

nZVI mobility and reactivity is improved using polyelectrolytes, polymers, surfactants, or supports (as clay) which provide steric and electrostatic stabilization against the particle-particle attractive forces limiting nZVI aggregation. In comparison to nZVI "coating" strategy, the nZVI stabilization by support allow a direct contact with the pollutant, reducing the electron path from nZVI to the target contaminant increasing nZVI reactivity. However, even if the nZVI dispersion at the support surface is efficient, the supported nZVI mobility is limited by the support materials itself.

Among the family of cellulose derivatives, cellulose nanocrystals (CNS), derived from natural cellulose fibers by controlled acid hydrolysis, have emerged as a new class of renewable and cost effective nanomaterials. CNS with this high surface area and functionalizable surface makes them interesting nanoparticle supports. In addition, nanocellulose suspensions in water are very stable and could confer enhanced stability and mobility to nZVI supported by them. In that way, we synthesize two CNS-nZVI nanocomposites (Fe/CNS weight ratio=1) with two different CNS functional surfaces (-OH and -COOH) using a classic sodium borohydride synthesis pathway. The final nanocomposites were characterized by XRD, XPS, FTIR and electron microscopy techniques. The properties reactivity of CNS-nZVI have been studied by methyl orange dye degradation and their mobility properties with transport through porous media. The CNS-nZVI show a significantly higher reactivity and mobility in comparison to bare nZVI. In addition CNS-nZVI reveal a higher resistance to oxidation.

Nanoscale zero valent iron impregnation of covalent organic polymer grafted activated carbon for water treatment

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Basil Uthuppu, Technical University of Denmark; Damien Thirion, Korea Advanced Institute of Science and Technology; Cafer Yavuz, Korea Advanced Institute of Science and Technology; Mogens Jakobsen, Technical University of Denmark; Henrik Andersen, Technical University of Denmark; Yuhoon Hwang, Seoul National University of Science and Technology

The use of nanoscale zero valent iron (nZVI) has quickly become a leading research material for the treatment of typically hard to degrade contaminants found in groundwater. These contaminants include antibiotics, pesticides, halogenated organics, heavy metals, among others. However, the effectiveness of nZVI has its limitations, due to its high reactivity and subsequent loss of degradative ability. Therefore, nZVI must be stabilized in a matrix allowing for the maintaining of reactivity, as well as the protection from the effects of the surrounding environment.

By employing a nanoporous polymeric network already previously proven to stabilize nZVI and a long-standing water treatment material, activated carbon; we have developed an advanced material that allows for the not only the stabilization of nZVI, but also the improved degradation of various water contaminants. This was done by performing a series of surface modification techniques to the surface of the activated carbon, then physically grafting the covalent organic polymer to the carbon in a shell-like manner, and ultimately synthesizing nZVI in situ within the pores of both the activated carbon and the polymeric network. Not only does this enhanced version of activated carbon utilize the outstanding adsorptive properties of both activated carbon and the polymeric network, but it also employs the degradation capability of nZVI. In this way, a new breed of materials is being developed, working in a synergistic manner for the purpose of the remediation of contaminants found in the groundwater.

We confirmed the existence of the polymeric shell with a variety of chemical characterization techniques; including Fourier transform infrared spectroscopy (FTIR), elemental analysis, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). We also monitored the degradation and/or adsorption of various contaminants (e.g. chlorinated organics like trichloroethylene and trichloroethane, and heavy metals like cadmium and nickel) to produce the kinetics of the interactions.

New approaches for remediation of chlorinated solvent contamination in groundwater using nanoscale zero valent iron

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Sourjya Bhattacharjee, Sai C. R. Rajajayavel

Two recent advances, from our recent research, that significantly enhance the reactivity of nanoscale zero valent iron (NZVI) to chlorinated solvents such as trichloroethene (TCE) will be presented. The first study shows that rhamnolipid (biosurfactant)-coated and palladium-doped-NZVI (RL-Pd-NZVI) when reacted with TCE in a water-immiscible butanol organic phase results in 50% more TCE mass degraded per unit mass of Pd-NZVI than in the aqueous phase. Furthermore the TCE was degraded with 7-fold faster degradation rate (k_r of 0.091 day⁻¹) in the butanol phase versus 0.013 day⁻¹ in the aqueous phase. RL-Pd-NZVI are preferentially suspended in water in biphasic organic liquid-water systems and we demonstrate that their rapid phase transfer can be achieved by transporting Pd-NZVI by creating water-in-oil emulsions in the butanol/TCE organic phase by addition of NaCl. The significant enhancement in reactivity is caused by a higher electron release (3e⁻ per mole of Fe⁰) from Pd-NZVI in the butanol phase compared to the same reaction with TCE in the aqueous phase (2e⁻ per mole of Fe⁰). XPS characterization studies of Pd-NZVI show Fe⁰ oxidation to Fe(III) oxides for Pd-NZVI reacted with TCE in the organic butanol phase compared to Fe(II)oxides in the aqueous phase, which accounted for differences in the TCE reactivity extents and rates observed in the two phases. The study suggests that using RL to cause phase transfer of Pd-NZVI or any other form of NZVI into a water-immiscible phase could lead to significantly faster TCE degradation. In the second study we show that sulfidation of NZVI enhances the rate of dechlorination of TCE, and the enhancement depends on the extent of sulfidation. Experiments where TCE was reacted with NZVI sulfidated to different extents (Fe/S molar ratios 0.62 to 66) showed that the surface-area normalized first-order TCE degradation rate constant increased up to 40 folds compared to non-sulfidated NZVI. Fe/S ratios in the range of 12 to 25 provided the highest TCE dechlorination rates, and rates decreased at both higher and lower Fe/S. In contrast, sulfidated NZVI showed significantly lower hydrogen evolution rate compared to that by unamended NZVI, suggesting that sulfidation suppressed corrosion reactions of NZVI with water. X-ray photoelectron spectroscopy analyses showed formation of a surface layer of FeS and FeS₂. The results suggest that under sulfate reducing conditions, the reactivity of NZVI will be greatly enhanced.

A Facile and Cost-Effective Method for Oil Recovery from Water under Environmentally Relevant Conditions Using Polymer-Coated Magnetic Nanoparticles

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Dr. Jamie R. Lead (Director of the Center for Environmental Nanoscience and Risk, University of South Carolina)

Oil spills in both marine and non-marine environments can have dramatic effects on the environment. Current oil remediation techniques are inefficient and may have deleterious environmental consequences. However, nanotechnology offers a new route to potentially remediate oil pollution. In this study, a cheap and facile hydrothermal method was developed to synthesize polyvinylpyrrolidone-coated magnetite nanoparticles to separate a reference MC252 oil from oil-water mixture under a wide range of environmentally relevant conditions.

Our results show that for the optimum NP concentration (17.6 ppm) and separation time (1 h), near 100% of oil was removed from oil-water mixture in the ultrapure water as measured by fluorescence spectroscopy. Based on gas chromatography-mass spectrometry (GC-MS) data, approximately 100% of lower molecular mass alkanes (C9-C21) and greater than 67% of C22-25 alkanes were removed.

For the same separation conditions, data showed essentially 100% oil removal from synthetic soft, hard and sea waters in the absence of natural organic macromolecules (NOM). Nearly 100% of C9-C20 were removed, although there is a slightly lower removal of the longer chain alkanes. The presence of NOM led to a statistically significant decrease in oil removal by acting as a competitive phase for either PVP or oil and reducing NP-oil interactions driven by hydrophobic effect of PVP coating. Ionic strength facilitated oil sorption presumably by enhancing magnetic separation of the oil-NP complex. Alteration of the separation conditions allowed optimal oil removal, with essentially 100% oil removal under most, but not all, environmental conditions.

Finally, the same type of NPs were used to study the application of high gradient magnetic separation (HGMS) technique for oil removal under a continuous flow system. Using high magnetic field (0.56 T) and 1 h mixing time, data show 91% and 86% oil removal and 94% and 83% NPs removal in the presence and absence of 100 mg of stainless steel wool, respectively. Under these separation conditions, GC-MS results show greater than 80% and near 100% removal of alkanes (C9-C22) in the experiment without and with stainless steel wool, respectively. Our study shows that these NPs are a cheap, facile and reliable technique for removing oil under a wide range of environmentally relevant conditions.

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Poster Session III
R-305

Nanomaterials and Worker Safety: An Industrial Hygiene Perspective

Charles Koch, Robson Forensic, LLC

What is the health effect of employees who use nanomaterials in research or production processes? Workers are exposed to nanoparticles through inhalation, dermal contact, or ingestion, depending upon how employees use and handle them. Although the potential health effects of such exposure are not fully understood at this time, scientific studies indicate that at least some of these materials are biologically active, may readily penetrate intact human skin, and have produced toxicologic reactions in the lungs of exposed experimental animals.

Current research indicates that the toxicity of engineered nanoparticles will depend on the physical and chemical properties of the particle. Engineered nanomaterials may have unique chemical and physical properties that differ substantially from those of the same material in bulk or macro-scale form. Properties that may be important in understanding the toxic effects of nanomaterials include particle size and size distribution, agglomeration state, shape, crystal structure, chemical composition, surface area, surface chemistry, surface charge, and porosity.

A basic summary of the research related to worker safety will be presented.

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Poster Session III
R-306

Nanomaterials and Converging Technologies: Scenario in Risk Assessment, Safety and Security by Design

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From a technology standpoint, nanomaterials offer significant advantages due to their unique characteristics resulting from reduced dimensionality. Furthermore, advances in material synthesis have provided the means to control or even manipulate the transitional characteristics. Consequently, various "designer" materials with desired properties have recently been fabricated. Dual-use nature of technology coupled with the ability to functionalize with a plethora of biological configurations pose a significant safety and security concerns. Furthermore, a life cycle analysis of nanomaterials is largely unknown; and nanomaterials resulting from the laboratories, manufacture, and even incidental events pose serious concerns. Too little is known about the release of nanosized by-products from nanomaterials-waste after incineration at the end of their life-cycle. As an example, aquatic contamination occurs for multiple reasons ranging from taking the water sources for granted, negligence in waste disposal, deliberate contamination, and technological innovations outpacing development of effective guidelines for life-cycle management and regulations to properly recycle/reuse/disposal of commercial nano-products. Notwithstanding such concerns, the beneficial uses of nanomaterials offer a challenging scenario for policy-makers, researchers, and industrialists alike to propose and implement viable alternatives for sustainable development in terms of keeping up with the latest technological innovations, social responsibility, and "being green". With so much at stake, it is prudent to challenge conventional wisdom and investigate a new set of strategies that employ nexus of technological innovations, in conjunction with "acceptable" risk assessment and a strategic transformation in "use, reuse, and recycle" as effective management tools to address "design safety, security, and sustainability". "Safety and Security by design" employ strategic transformations towards ensuring that humans and a safe environment can simultaneously exist on the Earth. We have investigated life-cycle-assessment based on the characterization, assessment, and management of risk to assess impacts on human and environmental health from a safety and security standpoint. We present strategic solutions to a life-cycle-based approach to nanomaterials and potential toxicity of nanosized particles using model of the sea urchin *Paracentrotus lividus*, Zebra Fish and their offspring. Passage through membranous barriers via the digestive tract to the coelomic fluid is the subject of ongoing study using biomarkers, such as coelomic fluid inside coelomocytes

(uptake), cholinesterase activity, and using expression of stress-related proteins (HSP70) and Gonads morphological features. Aquatic (nano)ecotoxicity is arguably the least understood and requires systematic investigation. Ongoing research aims to detect, counter, and mitigate potential security threats and is at the core of our current and ongoing investigations, hence we further present a strategic thrust to identify, assess, and recommend revolutionary strategic solution pathways using field-ready technologies, and foresight tools, already developed by the authors, to offer possible solutions pathways.

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Poster Session III
R-307

Attenuated Total Reflection FTIR for in situ measurements of supported lipid bilayer formation and interaction with nanomaterials

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1Arielle C. Mensch, 1Marco D. Torelli, 1Madeleine M. Meyer, 1Joel A. Pedersen,
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Nanomaterials are becoming ubiquitous components in various technological devices and consumer products, which will no doubt lead to their release into the environment. Nanomaterials are likely to come in contact with biological systems such as eukaryotes, with the first interaction between the two occurring at the cellular membrane. Gaining molecular level insight into the association of nanomaterials with cell membranes of live cells is difficult, considering the inherent complexity of the cell surface. Supported lipid bilayers (SLBs) are used as model cell membranes to study their interaction with nanomaterials and provide insights as to what happens at the cellular membrane. We use polarized Attenuated Total Reflection (ATR) FTIR as an in situ technique to probe molecular level interactions between phospholipid SLBs and nanomaterials in solution. Supported lipid bilayer formation via vesicle fusion on oxidized silicon surfaces is well known, but silicon strongly absorbs in the spectral regions of interest. We discuss our approach to optimize this technique on a ZnSe internal reflection element, which has a wider transparent window in the infrared. Other optimization conditions, such as flow cell geometry and vesicle concentrations will be discussed. ATR FTIR is helpful at elucidating mechanistic understanding of interactions at the nano-bio interface, as shifts of the methylene stretching peaks between 2840-2960 cm^{-1} can report on changes in membrane fluidity as a consequence of nanoparticle binding. Additionally, shifts or attenuations of peaks between 960-1500 cm^{-1} corresponding to functional groups on the lipid head can be correlated to the specific chemical moieties that nanoparticles are bonding to. Studies using technologically relevant battery cathode nanomaterials, such as nickel manganese cobalt oxide (NMC), will be discussed.

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R-308

Colloid facilitated transport of cesium through heterogeneous porous media

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Mobility of contaminants in the subsurface has been known to be facilitated by mobile nano-colloids transport with groundwater. This is a concern as it can lead to more and faster spreading of contamination in environmentally sensitive waters. For example, environmental releases of contaminants such as radioactive cesium (^{137}Cs) have been reported at locations such as the Hanford site near Richland, Washington. Using 50 mg L^{-1} of $1\text{-}\mu\text{m}$ colloids with 0.5 mM of total Cs concentration and a bead-packed column (0.75 cm diameter by 10 cm long), we investigated the influence of colloid facilitated Cs transport under varying physicochemical porous media conditions: 1) homogeneous average $550 \mu\text{m}$ glass beads, 2) physical heterogeneity with average $550 \mu\text{m}$ glass beads and average $350 \mu\text{m}$ glass beads mixed randomly and/or layered, and 3) chemical heterogeneity with hydrophilic glass beads randomly mixed with hydrophobic beads of the same size. Colloid transport was shown to be retarded by the physical heterogeneity of porous media and did not have an initial breakthrough until close to 40 pore volumes (PV), and yielded 33-44% of total colloids recovery compared to homogeneous bead column with an initial breakthrough of 11 PV and 100% colloid recovery. The initial breakthrough of colloids for the chemical heterogeneity column was similar to the homogeneous column (13 PV), but yielded a recovery of 11% of total colloids introduced into the column. These combined results suggest that the silicate-based porous media can significantly reduce Cs transport associated with colloids, and that slight changes in the physical and chemical heterogeneity in the surrounding matrix will further reduce Cs facilitated transport by influencing colloid mobility.

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Visualize and measure the distribution of Titanium Dioxide Nanoparticles on the model rough surfaces using the Generalized Ellipsometry based birefringence imaging technique.

Negin Kananizadeh, University of Nebraska-Lincoln
Negin Kananizadeh, Darin Peev, Tino Hofmann, Mathias Schubert, Eva Schubert, Shannon Bartlet-Hunt, and Yusong Li

Understanding the interactions between engineered nanoparticles and soil/sediment surfaces is very critical to assess their potential environmental impacts. Large quantities of Titanium dioxide nanoparticles (TiO₂NPs) are released into the environment. Measuring the interactions between TiO₂NPs and natural substrates (e.g. soils and sediments) has been very challenging due to highly heterogeneous and rough natural surfaces. In this work, an engineered controllable rough surface known as three-dimensional nanostructured sculptured columnar thin films (SCTFs) has been used to mimic surface roughness. SCTFs possess optical anisotropy (birefringence). Attachment of TiO₂NPs on the surface of SCTFs changes the optical birefringence of SCTFs, which can be detected using Generalized Ellipsometry (GE) technique. We nano-plotted small known mass of 162, 354, and 1257 fg/m² of label-free TiO₂NPs on the surface of patterned N-shaped SCTFs. With the help of a new anisotropic contrast microscopy imaging (ACMI) device the measured intensity data were converted to 11 Mueller matrix elements to observe the distribution of TiO₂NPs. The areal mass density of TiO₂NPs printed on SCTF surface were then quantified using intensity data measured by ACMI, and an appropriate GE model. The measurement of ACMI was calibrated by comparing the areal mass density data from GE with the known total TiO₂NPs areal mass density printed on SCTF surface.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
R-310

Understanding the role of natural nanoparticles on the behaviour of PFOS in soils

Yanju Liu, University of Newcastle

Yanju Liu, Cheng Fang, Ravi Naidu; affiliations: University of Newcastle and 2CRC for Contamination Assessment and Remediation of the Environment (CRC CARE)

Perfluorooctane sulfonate (PFOS) as a commonly detected perfluorinated compounds has been investigated for its occurrence, toxicity, bioaccumulation, and potential risks. Its partitioning in soil components are sparsely investigated, which can be influenced by various parameters, including organic content, pH, ionic strength, free iron content, electrostatic interaction, and surface area. Soil matrix is a potential sink for PFOS contamination. It is crucial to investigate the partitioning of PFOS between soil and soil solutions. Natural nanoparticles are reported to be responsible for the transport of many contaminants. However, the interaction of natural nanoparticle with PFOS are yet to be investigated.

In this study, we focus on the influence of soil natural nanoparticles which could be potential carrier for the transport of PFOS in soils. Five contrasting soils have been spiked with PFOS for its fractionation analysis. The organic content, mineralogical composition, particle size, surface area and porosity, and morphology have been investigated for each fraction, in particular in the range of 250 - 2000 μm , 50 - 250 μm , 5 - 50 μm , 1 - 5 μm , 0.1 - 1 μm , and < 0.1 μm . The results will provide information on the binding and potential release of PFOS in soil particle fractions varying in physio-chemical properties and mineralogy. This information will underpin our understanding of the fate and transport of PFOS in contaminated sites.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
R-311

Graphene oxide modified polyamide mixed-matrix membranes for water treatment

Adam Inurria, Arizona State University
Dr. Francois Perreault, Mr. Doug Rice

Graphene-based materials can bring innovative solutions to the current limitations of water treatment technologies. In membrane processes, integration of graphene oxide in the design of membrane materials was shown to enable improved transport properties and increased fouling resistance. These novel properties are being imparted to membrane filtration practices in the form of mixed matrix membranes combining graphene oxide and polymeric materials. In this process, fine tuning the oxygen content of graphene oxide can improve both water permeation through graphenic structures and fouling potential of the membrane. This study focuses on development of mixed-matrix membranes using graphene oxide of different physicochemical properties. Graphene oxide was produced using different oxidation procedures and embedded in mixed-matrix membranes. The transport properties and fouling propensity of the produced membranes were characterized and compared. This study hopes to provide insight from graphene oxide synthesized through different methods in the development of a functioning mixed-matrix membranes with graphene oxide, and highlight the role of the oxidation state of the material in the performance of the membrane.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
R-312

Quantifying multi-walled carbon nanotube removal at wastewater treatment plants from association with activated sludge by tracking the residual trace element Yttrium

Justin Kidd, Arizona State University
David Hanigan, Jared Schoepf, Paul Westerhoff

Information on the affinity of nanoparticles for suspended solids is needed to assess the possibility of their removal by wastewater treatment systems. Our research was conducted in three phases: (1) to generate experimental data on the quantification of multi-walled carbon nanotubes (MWCNTs) through single particle ICP-MS and ICP-MS by tracking the residual trace element Yttrium, (2) to determine the association of trace metals to MWCNTs, and (3) to simulate MWCNT removal via association with wastewater biomass. Major key findings from our study show that Yttrium was a stable and representative marker for the MWCNT at environmentally relevant concentrations and could be used to obtain a detection limit below 0.05 mg/L of MWCNT. TEM imaging showed that the trace metal catalysts were physically bound to the MWCNT in bundles. Using a range of typical wastewater biomass concentrations between 0.5 and 5.0 g TSS/L, environmentally relevant MWCNT doses of 0.1 and 0.5 ppm results in less than 50 ppb of MWCNT in the supernatant after three hour contact times. Based upon the data found, we can begin to predict effluent discharge MWCNT concentrations from a variety of commonly used activated sludge processes

Nanomaterial fate in seawater - a rapid sink or intermittent stabilization?

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Oceans and seas are exposed to the release of nanomaterials through indirect routes: e.g. waste-water treatment plant effluent discharge, atmospheric deposition and direct routes: e.g. shipping, solid waste disposal, or other human activities. The environmental fate of nanomaterials is governed by their surface chemistry and the physicochemical properties of the surrounding media. In aqueous systems, nanomaterials are considered to be relatively stable when the ionic strength of the water is low, and/or when the presence of organic matter is combined with low concentrations of divalent ions. Therefore, it is generally perceived that nanomaterials are more likely to be stable in lakes, rivers, and groundwater aquifers; in seas and oceans, where the ionic strength is significantly higher, it is expected that they would quickly aggregate and settle on the sediments. However, seas and oceans, being the largest water bodies of the earth, are hosts to some of the most vital and large scale biogeochemical processes for biota and these processes involve transformations of a large proportion of the earth's carbon cycle. For example, nutrient availability combined with increased sunlight and temperature in the spring trigger a rapid growth of phytoplankton and microorganisms (spring bloom), which in turn triggers zoo plankton grazing and viral activity, which lead to dissolved organic matter release through exudates, sloppy feeding and cell lysis. Such seasonal production and following transformations of dissolved and colloidal organic matter could influence particle stability and the fate of nanomaterials in seas and oceans.

It is especially the extracellular polymeric substances (EPS) in the form of nanofibrils that can influence associated nanomaterials in two ways. Although we know that under the influence of turbulence, EPS will form gel-like aggregates with other forms of SPM to form settling transparent exopolymeric particles (TEP) also called marine snow, previous studies of natural nanomaterials indicate intermittent stabilization by the EPS. In this work we test the hypothesis that organic matter produced during the spring bloom may act as steric stabilizers for nanomaterials and overcome the suppression of electrostatic repulsion that is caused by the high ionic strength of the water. We use sea water collected from the Gullmarn Fjord, Swedish west coast, during the spring bloom of 2016 and test the stability of gold nanoparticles in the $\mu\text{g/L}$ concentration range. Overall, we find a stabilizing effect of the sea water and compare our results to artificial sea water typically used in lab-scale experiments.

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Poster Session III
R-314

Application of single particle ICPMS for tracking iron nanoparticles at environmental relevant concentrations

Jana Navratilova, US EPA

Increased concerns over the release of engineered nanomaterials from consumer products has increased the need for analytical methods capable detecting the released nanomaterials across their life cycle at very low concentrations (ppt range). Currently one of the most promising analytical techniques used to track metallic engineered nanoparticles not only in the environmental samples is single particle ICPMS (spICPMS). SpICPMS analysis can provide more information than other techniques commonly used for nanoparticle characterization, including particle number concentration, particle mass and the concentration of dissolved metal. Metal oxide nanoparticles are of particular interest because of their large scale production that raises concerns about their release, exposure, fate and impact on the environment. In this contribution spICPMS is used to study potential release of Fe₂O₃ nanoparticles from consumer products into simulated aquatic media of different compositions. The spICPMS method was optimized using in house synthesized and characterized iron nanoparticles and then applied to the analysis of leachates.

Wednesday, August 16/Thursday, August 17, 2016
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R-315

Application of Single Particle ICPMS to detect and characterize TiO₂ in rice (*Oryza sativa* L.) plants exposed to nanoparticle and bulk particle TiO₂

Katie Challis, CSM

Katie Challis (a), Yingqing Deng (b), Savelas Rabb(c), R. David Holbrook(c), Bryant C. Nelson(c), Baoshan Xing(c), James Ranville(a), Elijah Petersen(c)
.Affiliations (a)-Colorado School of Mines, (b) Stockbridge School of Agriculture, (c) National Institute of Standards and Technology

Titanium dioxide (TiO₂) nanoparticles are one of the most common nanoparticles in consumer products. The particles are incorporated into products such as sunscreens, "self-cleaning" concrete, and paint as well as in toothpaste and food products. The ubiquity of the TiO₂ in products is a cause for concern due to the inevitable release into the environment and eventual presence in agricultural areas. To investigate if TiO₂ particles could be taken up by crops, rice plants (*Oryza sativa* L.) were exposed to two different TiO₂ particles: nanoparticles (NIST SRM 1898) and bulk TiO₂ (Acros Organics) at 50 ppm TiO₂ concentrations in hydroponic pots for one week. Plants were harvested and dried prior to digestion and subsequent sp-ICP-MS analysis. Two digestion methods were used to destroy plant material and free any TiO₂ present in the plants. The first method was an enzymatic digestion using Macrozyme enzyme to break down plant material. The enzyme did not achieve complete digestion. The second method was a microwave acid digestion method which successfully destroyed plant material. Single particle-ICP-MS (sp-ICPMS) was used to analyze the digested suspensions to determine TiO₂ size and size distribution. In the enzymatic digestion, nanoparticles in plants were 44 ± 31 nm and the bulk particles exposed plants did not release a sufficient number of nanoparticles to accurately determine a size and size distribution. In the acid digestion, the mode size of particles was 65 ± 53 nm and 236 ± 67 nm in plants exposed to nanoparticle TiO₂ and bulk TiO₂, respectively. Particle size results suggest that the TiO₂ was resistant to dissolution even under the extreme microwave conditions.

Ecotoxicology and Bioavailability

Oral Presentations



Monday, August 15, 2016
Ecotoxicology & Bioavailability I
1:50 PM

Influence of surface functionality on Apolipoprotein and nanosilver biocorona

Achyut Raghavendra, Clemson University
Jonathan Shannahan, University of Colorado Denver; Jared M Brown, University of Colorado Denver; Ramakrishna Podila, Clemson University

It is beginning to be recognized that formation of a biocorona is critical to the biological interactions of engineered nanomaterials (ENMs). Upon introduction into a biological system, ENMs rapidly associate a variety of macromolecules including proteins, peptides, amino acids, fatty acids, lipids and other organic matter forming a biocorona. The formation of the corona is not only dictated by the physicochemical properties of the ENM but also the composition of the physiological environment. ENM-biocorona with apo-lipoprotein A1 (apoA1), a vital component of HDL, may increase the risk of myocardial infarction in patients with obesity. Here, we will present the influence of surface functional groups on Ag nanoparticles on the formation of apoA1 biocorona and the associated immune response. In particular, we show that the amount of protein adsorption and protein secondary structural changes are highly dependent on the surface functionality.

Monday, August 15, 2016
Ecotoxicology & Bioavailability I
2:10 PM

Environmental nanosafety: lessons learnt

Teresa Fernandes, Heriot-Watt University

The interest in the environmental effects of emerging contaminants continues to increase due to lack of knowledge on their use, fate and effects, but also the lack of techniques necessary for monitoring their occurrence in the environment. Once such group of emerging environmental contaminants are engineered nanomaterials (ENMs). The interest in these materials is continuing to grow along with the increasing number of applications of nanotechnology. Although availability of data continues to increase, the focus is still on a narrow range of species with little attempts to compare effects across species and how exposures in realistic environmental conditions may affect bioavailability and hazard. In this presentation, the results of exposures of a range of nanomaterials, with different modifications and functionalisations, will be compared across different environmental conditions and species. This presentation will provide a summary of the state of the art on the occurrence of specific ENM effects in biological systems; differentiate cells/tissue injuries due to nano and non-nano materials and between ENMs with similar chemistry but different physical properties, comparing studies of pristine ENMs in static conditions with more realistic scenarios. Results from this work contribute to current developments in the field including the derivation of read-across and cross taxa and endpoints comparisons.

Monday, August 15, 2016
Ecotoxicology & Bioavailability I
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Uptake, subcellular distribution, and translocation of differentially charged CeO₂ nanomaterials in *Solanum lycopersicum* cv Micro-Tom (tomato).

Jieran Li, University of Kentucky

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4. Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL

The objective of this on-going project is trying to understanding the role of polymer coating charge on the uptake, translocation and subcellular distribution of CeO₂ in the tomato (*Solanum lycopersicum* cv Micro-Tom). Dextran (DEX; neutral), diethylaminoethyl dextran (DEAE; positive) and carboxymethyl dextran (CM; negative)-coated CeO₂NP (3-5 nm primary particle size) are synthesized and characterized for primary particle size (TEM), hydrodynamic diameter (DLS) and zeta potential (PALS) in exposure media. Tomato seedlings grown in 10% Hoagland solution are exposed to DEAE, DEX and CM CeO₂NPs and control media for 2 weeks. The bulk tissue concentrations of Ce are determined in shoots, leaves alone and roots by inductively coupled plasma mass spectrometry (ICP-MS). Tissues are also collected from the root tip region and prepared by thin sectioning for Ce mapping using a synchrotron based X-ray fluorescence nanoprobe (nXRF) using the hard X-ray nanoprobe (HXN) at the National Synchrotron Light Source-II (Upton, NY, USA). The results indicate that CeO₂NP with positively charged coatings have the greatest impact on seedling growth. There is a trend of decreasing values of bioconcentration factor for all three CeO₂NP with increasing exposure concentration. Ce is concentrated mostly in the root tissue although there is significant translocation of Ce from the roots to shoots. The distribution of Ce in the root tip cells (down to 10-15 nm resolution) vary with the charge states of the coatings, with the apoplastic spaces showing the highest Ce accumulation, suggesting an apoplastic uptake mechanism. Entry into the root tip appears to occur in gaps between cells in the epidermis formed as cells are being shed from the root tip. Dissolution data showed that there is minimal Ce dissolution from the particles in the nutrient media used in the study. As the first general users of HXN, which is the highest resolution X-ray fluorescence microscope in existence, this study provides perhaps the highest resolution X-ray fluorescence imaging of nanomaterials in a biological tissue to date.

Monday, August 15, 2016
Ecotoxicology & Bioavailability I
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Cross species comparison of the impacts of nanomaterials: the role of molecular level differences due to environment and organism

Rebecca Klaper, University of Wisconsin-Milwaukee

Our current understanding of the potential toxicity of nanomaterials differs depending on not only the chemical composition of the nanomaterial but with the biological system being tested. This may be due to not only the environment in which the organism is tested but also the molecular variation across organisms. In the Center for Sustainable Nanotechnology we are investigating how the chemistry of the environment and chemistry of the organism play a role in the molecular interaction of the organism and nanomaterial. In this talk I will discuss comparisons of impacts made across two types of nanomaterials, model nanoparticles, gold with positively or negatively charged ligands, as well as the commercially relevant new nanoparticle-based battery materials and a variety of test species representative of aquatic and sediment dwelling organisms. Differences in impacts due to the test media, representative of different environments, will be discussed with respect to organic matter content, proteins and ionic strength. In addition, comparisons will be made across species with respect to cellular chemistry and their respective molecular responses and how they differ with respect to instigation of pathways dealing with metabolism, immunology, reproduction and others. We show that surface charge, size, and specific metal species composition play a role in molecular scale interactions with the organism and lead to changes in multiple biochemical pathways. However there are species-specific differences that impact the ability to draw the same conclusion across organisms and systems. The implications of these results towards developing principles of sustainability for nanomaterials will be discussed.

Monday, August 15, 2016
Ecotoxicology & Bioavailability I
3:10 PM

Nanotechnology-based Technologies for Sustainable Food Production

Gregory Lowry, Carnegie Mellon University
Sonia Rodrigues

The food, energy and water (FEW) nexus is under enormous pressure from population growth, increasing global food demand, and increasing fresh water withdrawals and energy consumption. These are exacerbated from food waste, inefficient use of agrochemicals, environmental degradation and climate change. Transformative, system-level solutions to the inefficiencies are necessary for promoting sustainability at the FEW nexus. This presentation identifies and discusses the highest value near-term opportunities for nanotechnology to help minimizing resource inputs for food production including minimizing food waste, and the significant scientific and engineering challenges to being able to realize the promised benefits. This analysis is based on the outcomes of an interdisciplinary National Science Foundation workshop that gathered ~50 experts from the U.S. and the EU in the areas of nanotechnology, energy, water, agriculture, systems engineering, data integration and analysis, and social science.

Specific properties of nanomaterials such as large surface to volume ratios and surface activity; physical (e.g. optical and electronic) properties; superparamagnetism or confinement effects resulting from the nanoscale dimensions can favor several applications in agro-food systems. There include for example sensitive detection of moisture, pH, temperature, pathogens or chemical substances; food safety and food waste minimization; distributed water treatment; resource recovery; targeted delivery of agrochemicals; or animal health surveillance and control. However, where existing, nano-enabled applications are still at very early stages of research and development and in most cases testing in real soil, food or water systems is lacking. Realizing nanotechnology benefits will require overcoming scientific challenges to develop selective, sensitive, durable materials, and overcoming engineering challenges for the development of system-level platforms. In addition, technoeconomic gap analysis is needed to identify highest-value opportunities and to develop cost-effective and safe applications, and societal (risk perception and communication) and regulatory challenges must be addressed.

Tuesday, August 16, 2016
Ecotoxicology & Bioavailability II
3:50 PM

Metal analysis contained in Single Cells using Single Particle ICP-MS: quantifying both exposure and dose of gold and silver NPs to freshwater alga

Ruth Merrifield, University of South Carolina
Dr Chady Stephan (Manager-Global Applications-Nanotechnology, 6 - 501 Rowntree Dairy Rd, Woodbridge, ON L4L 8H1, Canada) and Dr Jamie Lead (Center for Environmental NanoScience and Risk (CENR) Arnold School of Public Health University of South Carolina, USA)

Exposure and dose of nanoparticles (NPs) to cells is a topic of considerable importance in nanotoxicology and related areas. Accurate analysis of concentrations in exposure media and in organisms is not easy and sometimes impossible with current technologies due to issues of separation of ion and particle, the transformation of NPs in aqueous media and biological tissue and other challenges. Even mass concentrations are not measured easily and the literature is replete with examples of poorly measured or unmeasured NP concentrations after hazard experiments. Mass concentration is the most used metric, although considerable attention has been paid in principle to other metrics, which have been extremely difficult to quantify accurately. Here we exposed three strains of freshwater algae cell to Au and Ag NPs and ions, including core-shell NPs. We show that single particle ICP-MS (SP-ICP-MS) was able to measure the number concentration (and other parameters) of NPs in the suspension media, the number of cells containing metal (% uptake) and the concentration of metal within those cells in the three species. Additionally, differentiation between ion and NP concentration within the cell is possible. We show that for constant exposure conditions, uptake is dependent on the algal species.

Tuesday, August 16, 2016
Ecotoxicology & Bioavailability II
4:10 PM

Metabolomics as an early indicator of potential implications from engineered nanomaterials

Arturo Keller, University of California, Santa Barbara
Lijuan Zhao

While significant progress has been made in understanding the potential acute toxicity of many engineered nanomaterials (ENMs), predicted environmental concentrations are for the most part well below the levels that may cause acute toxicity. Metabolomics may provide an early indicator of the potential implications of ENMs, by signaling early on whether exposure to an ENM results in up- or down-regulation of specific metabolites. Here we present a study of the metabolic response of a crop plant to exposure to nano-Cu, which shows that production of over 120 metabolites are influenced by this ENM. These results are correlated with uptake of Cu into the plant and physiological changes. This information also provides a tool for determining whether an ENM is bioavailable within the soil or aqueous matrix, since organisms may exhibit early changes in their metabolic profile.

Tuesday, August 16, 2016
Ecotoxicology & Bioavailability II
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Fish gastrointestinal systems alter the sorption of organic contaminants to single-walled carbon nanotubes

Joseph Bisesi, University of Florida

Ngo, T1, Castillo, B1, Lavelle, CM1, Robinson, SE1, Crosby, H1, Saleh, NB2, Ferguson, PL3, Denslow, ND4, Sabo-Attwood, T1. 1Department of Environmental and Global Health, Center for Environmental and Human Toxicology, University of Florida, Gainesville, FL, USA 2Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, Austin, TX, USA. 3Department of Civil and Environmental Engineering, Nicholas School of the Environment, Duke University, NC, USA. 4Department of Physiological Sciences, University of Florida, Gainesville, FL, USA

Increases in production and commercial use of single-walled carbon nanotubes (SWCNTs) may lead to release of these materials into aquatic environments. While SWCNTs have been shown to be fairly inert, these materials exhibit high sorption affinity for hydrophobic contaminants that may already be present in aquatic environments. While it has been hypothesized that these interactions may reduce oral bioavailability, recent evidence from our laboratory suggests that sorbed contaminants may still be bioavailable. The synthetic estrogen, ethinyl estradiol (EE2), sorbs to SWCNTs with high affinity, but these mixtures still cause binding and activation of the estrogen receptors *in vitro*, indicating that sorbed EE2 maintains bioactivity. To determine if these results translate to downstream responses in fish, both largemouth bass and fathead minnows were orally exposed to mixtures of SWCNTs and EE2 and hepatic vitellogenin mRNA expression was measured as a biomarker of EE2 exposures. Results indicate EE2 does not stay sorbed to SWCNTs in fish gastrointestinal systems, irrespective of gastrointestinal physiology. Current research is focused on understanding the mechanism of desorption of EE2 from SWCNTs in the gastrointestinal system by using radiolabeled binding assays. Results from this study further our understanding of interactions of SWCNTs and contaminants already present in our aquatic environments which is essential for determining the potential organism and ecosystem health risks of these materials.

Tuesday, August 16, 2016
Ecotoxicology & Bioavailability II
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Development of graphene-based antimicrobial coatings: towards an understanding of the antimicrobial mechanisms to guide material development

Francois Perreault, Arizona State University

Graphene oxide possesses attracting properties for the design of novel antimicrobial surfaces due to its contact-based antimicrobial activity. Graphene-based antimicrobial materials have already found promising applications in multiple fields, from biofouling-resistant membranes in water treatment to antimicrobial fabrics and polymers for biomedical materials. However, the mechanisms of antimicrobial activity of graphene are still a matter of debate, which limits the efficient design of graphene-based antimicrobial applications. In this work, we demonstrate the importance of oxidative stress in the antimicrobial activity of graphene oxide surface coatings, and investigate how the physicochemical properties of graphene oxide sheets can be tuned to optimize their antimicrobial activity. For graphene oxide-coated surfaces, decreasing sheet size is found to increase bacterial inactivation. This size-dependent change in the antimicrobial activity of graphene oxide is related to changes in the material structure that increase its oxidative capacity. Using glutathione oxidation by graphene oxide and toxicity mitigation by antioxidant molecules, the size-dependent bactericidal effect of graphene oxide is shown to be primarily due to oxidative mechanisms. These findings shed light on the fundamental mechanisms of antimicrobial interactions of graphene oxide.

Wednesday, August 17, 2016
Ecotoxicology & Bioavailability III
9:30 AM

Interactions between Fe-doped imogolites nanotubes and the soil bacteria *P. Brassecaeearum*.

Armand Masion, CNRS-CEREGE
A. Avellan, C. Levard, C. Santaella, W. Achouak, J. Rose

Imogolites are naturally occurring alumino silicate nanotubes. Their Ge analogues can readily be obtained with good control over length, wall multiplicity and doping. Here we describe the interactions of Fe doped imogolite and the rhizosphere bacteria *P. Brassecaeearum*. While non doped nanotubes caused toxic effects, this toxicity was alleviated when approx. 1% of Fe was incorporated into the tube wall. We observed Fe uptake by the bacteria mediated by the release of siderophore into the medium. The interaction between tubes and bacteria were monitored by hyper-spectral imaging, and X-ray tomography gave closer insight into the fate of NP in a simulated rhizosphere.

Wednesday, August 17, 2016
Ecotoxicology & Bioavailability III
9:50 AM

Delineation of Toxicity of Transition Metal Oxide Nanoparticles: What matters most?

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Transition metal oxide nanoparticles (NPs) in the Fourth Period of the Periodic Table of Elements are popular nanomaterials in industrial and biochemical applications. In this study, we established a unique trend of three-tiered cytotoxicity induced by seven metal oxide NPs: low (TiO₂, Cr₂O₃ and Fe₂O₃), moderate (Mn₂O₃ and NiO) and high (CuO and ZnO). As atomic numbers increase, cytotoxicity increases. NPs were able to elevate oxidative stress and perturb intracellular calcium homeostasis via multiple signaling pathways leading to reduction of cell viability, alteration of cell cycle and inhibition of cell proliferation. We further asked the question: what are the physicochemical properties of NPs that dictate observed toxicity? Using a variety of analytical tools and theoretical approach, we conclude that particle surface charge, metal dissolution, and the relative number of binding site on NP surface explain differential cytotoxicity observed. Band-gap energy seems not a contributing factor. Collectively, our study contributes to the understanding of molecular mechanisms of NP-induced toxicity. Moreover, the delineation of independent factors of NPs that govern toxicity helps design of safer NPs in the future.

Wednesday, August 17, 2016
Ecotoxicology & Bioavailability III
10:10 AM

Goldfish (*Carassius auratus*) immune responses to intravenously injected polymer-coated TiO₂ nanoparticles.

Van Ortega, University of Alberta

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Greg Goss^{1,2} 1.Department of Biological Sciences, University of Alberta
2.National Research Council (Canada), National Institute for Nanotechnology,
University of Alberta, Canada 3.School of Biological Sciences, Plymouth
University, UK

Evidence of nanoparticle (NP) effects on immune cell function has been demonstrated using in vitro models in previous studies that report both the over-activation of pro-inflammatory responses, and suppression of others. Our group has also demonstrated modified immune effects for both cell lines and isolated primary goldfish neutrophils when exposed in vitro to polymer-coated metal-oxide NPs. However, the translation of these effects to in vivo models has not yet been explored. Despite a lack of information of in vivo immune effects, it has been shown that when NPs enter circulation in fish, the vast majority is deposited into kidney and spleen tissues, which in fish are the major hematopoietic organ and where many innate immune cells reside. Thus, there is an increased opportunity for neutrophils and macrophages in these organs to interact and be affected by tissue-accumulated NPs. In this study we have sampled kidney and spleen tissues and isolated kidney neutrophils and macrophages at 0, 1, 7, 14 and 28 days from mature goldfish (*Carassius auratus*) injected with either polymer-coated TiO₂ (1 µg/g) or Cortland's saline (control). Preliminary results show significant and long-term deposition of Ti metal in the kidney and spleen, increased kidney and spleen tissue damage, increased responsiveness of kidney neutrophils and changes in the expression of various pro- and anti-inflammatory related genes in TiO₂-injected fish. We also show a differential response in the capacity of TiO₂-exposed fish to clear a known pathogen during a 28-day infection challenge. Results from our study demonstrate that NP exposure can significantly impact a fish's capacity to appropriately activate numerous immune functions during an infection and this may affect their long-term health and viability.

Wednesday, August 17, 2016
Ecotoxicology & Bioavailability III
10:30 AM

Effect of cysteine on bioavailability of Ag from Ag nanoparticles to a freshwater snail

Samuel Luoma, University of California Davis
Marie-Noëlle Croteau, U. S. Geological Survey

If released into the environment metal-based engineered nanomaterials (Me-ENMs) are likely to undergo numerous transformations that will affect their bioavailability, toxicity and ecological risk. Interactions with dissolved organic material drive one of the most important classes of transformation, although the outcomes of those interactions are complex and sometimes appear contradictory. Here we model the drivers of silver bioaccumulation at environmentally realistic concentrations (25nM) from two types of coated silver nanoparticles, PVP AgNPs and PEG AgNPs, in the presence of either Suwannee River humic acid or a high-affinity thiol-rich organic ligand, cysteine using the freshwater snail *L. stagnalis* as a model organism. Uptake rates of dissolved silver released from the NPs were quantified with and without cysteine, in experiments with silver nitrate (AgNO₃). The contribution of dissolved Ag to uptake from AgNPs with two different polymeric coating was determined from dissolved Ag concentrations and from AgNO₃ uptake rates. Uptake attributable to particulate AgNP was determined by difference from overall uptake. Overall uptake of Ag from the two NPs either increased or was not strongly affected in the presence of 1 × 10 mg/L humic acid. It was substantially reduced by addition of equimolar 1 Ag: 1 cysteine, but not eliminated. Uptake of dissolved Ag also was reduced but not eliminated. In the absence of cysteine, a definitive component of uptake into tissue from the AgNPs themselves was observed. The rate of particulate Ag uptake differed with the type of polymer coating. With the addition of equimolar cysteine (1 Ag: 1 cysteine) the uptake rate of particulate PVP-AgNP uptake was reduced and PEG-AgNP uptake was eliminated. These results suggest transformations that affect bioavailability differ depending upon the nature of the natural organic material and the type of polymer coating used to stabilize the AgNP. Humic substances contain relatively few strong ligands for Ag so their effects on uptake of Ag from NPs was limited.

Wednesday, August 17, 2016
Ecotoxicology & Bioavailability III
11:20 AM

Microbial toxicity of Ga₂O₃, In₂O₃, GaAs, and InAs nanoparticles in semiconductor manufacturing effluents

Chi Nguyen, The University of Arizona
Dr. James Field, The University of Arizona; Dr. Reyes Sierra-Alvarez, The University of Arizona

In the State of Arizona, semiconductor manufacturing is an important industrial sector which requires significant amounts of water for processing. One of the processes with the highest water demand is chemical mechanical planarization (CMP), a step used to polish wafer surfaces into ultra-flat surfaces through a combination of physical and chemical forces. The CMP process utilizes slurries of abrasive nano-sized particles (NPs) such as alumina (Al₂O₃), ceria (CeO₂), and silica (SiO₂). Annually, millions of gallons of CMP waste are discharged to municipal sewers. Because III-V materials such as gallium arsenide (GaAs), indium arsenide (InAs), and gallium indium arsenide (GaInAs) can provide high electron mobility with wide and adjustable band gaps and reduce power consumption, the semiconductor manufacturing sector is planning to introduce III-V film structures into silicon wafers to enhance device performance. Aqueous solutions generated during the planarization of III-V films are expected to contain a mixture of metal oxides NPs as well as indium (In), gallium (Ga), and arsenic (As) species. The presence of toxic III-V species and NPs in CMP effluents is a concern. While the aquatic chemistry and ecotoxicity of arsenic species have been investigated extensively, essential information is needed for the environmental chemistry and ecotoxicity of other III-V species. Consequently, research is required to understand the speciation, adsorption, transport, and toxicity of III-V materials in natural water and engineered systems. This presentation will discuss the results of preliminary experiments conducted to investigate the microbial toxicity of nano-sized gallium oxide (Ga₂O₃), indium oxide (In₂O₃), GaAs, and InAs. These materials can potentially be formed during polishing operations of GaInAs films. Different tests were performed including the widely used commercial toxicity Microtox bioassay (inhibition of bioluminescence) as well as bioassays using microbial populations important in waste water treatment, specifically, anaerobic methanogenic microorganisms. The results obtained indicated that Ga₂O₃ and In₂O₃ NPs are not inhibitory at concentrations as high as 500 mg/L. In contrast, the GaAs and InAs NPs caused 50% methanogenic inhibition at concentrations of 5.7 and 129 mg/L, respectively. Additional experiments demonstrated that the main mechanism of GaAs and InAs toxicity is dissolution and release of toxic arsenic oxyanions (chiefly trivalent arsenite).

Thursday, August 18, 2016
Ecotoxicology & Bioavailability IV
1:50 PM

Positively charged nanoparticles lead to artifacts in a *C. elegans* toxicity assay

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Bustos Montoro, AR, Peterson, AW, Reipa, V, Scanlan, LD, Hosbas Coskun, S,
Cho, TJ, Hackley, VA, Petersen, EJ, Winchester MR, Elliott, JT

The unique properties of engineered nanoparticles (ENPs) may lead to unforeseen interactions in toxicity assays designed for soluble chemicals. Yet, there are a lack of test methods tailored to ENPs, which has hindered efforts to understand the consequences of ENP release. Here, we detail our efforts to adapt a *C. elegans* toxicity assay for ENPs, including a cause-and-effect analysis to identify sources of error. We found that shaking plates during the assay decreased growth by 36% and altering feed concentration greatly affected toxicity of a positive control. We also found that different media produced similar results in the toxicity assay, allowing for flexibility to suit ENPs. Additionally, we discovered that positively charged polystyrene nanoparticles (PSNPs) impact growth of *C. elegans*. However, those impacts were due to an interaction with *E. coli* that is used as feed in the assay and impacts on growth were more variable for PSNPs (52%) compared to the positive control (9%). We repeated this test using Au ENPs with coatings ranging from positive to negative and found similar results with our positively charged Au ENPs compared to PSNPs, however, no impact was found with neutrally or negatively charged ENPs. These artifacts led us to test these ENPs in toxicity assays that do not require *E. coli* and we found no toxicity associated with the positively charged ENPs. We conclude that either a different assay must be used to accommodate positively charged ENPs or adaptations to the current assay must be made to avoid the interaction.

Thursday, August 18, 2016
Ecotoxicology & Bioavailability IV
2:10 PM

Trojan Horse Mechanism and Localization explains Toxicity of Ni/SiO₂ Complex Engineered Nanomaterials

Sharlee Mahoney, University of Pittsburgh
Thomas Richardson, Ipsita Banerjee and Goetz Vesper

Despite evidence for potentially increased toxicity, functional nanomaterials are finding increasing application in a wide range of industrial processes and consumer products. Their toxicity has to-date have mainly been studied for bare nanoparticles (NPs). In contrast, complex engineered nanomaterials (CENs), a rapidly emerging class of nanomaterials to combat NP agglomeration and deactivation effects, have found little attention to-date.

We are investigating the toxicity associated with three carefully structured Ni/SiO₂ CENs which mimic common CEN configurations in industrial use: Ni NPs deposited externally on silica NP supports (Ni-SiO₂), embedded in non-hollow, porous silica NPs (nhNi-SiO₂), and encapsulated in hollow, porous silica shells (hNi-SiO₂). We hypothesize that encapsulation/embedding in porous shells will mitigate toxicity while still providing accessibility and functionality of the embedded metal NP. All CENs were thoroughly characterized structurally (TEM, XRD, BET) as well as for dissolution, aggregation, and settling properties. Toxicity was evaluated in comparison to an inorganic nickel salt (NiCl₂) using 24 hour cytotoxicity assays with 3t3 fibroblasts, a robust, inexpensive cell line that is a FDA standard test model for evaluating biomaterial safety and been increasingly used in nanotoxicity studies. Flow cytometry and fluorescence microscopy (using tagged CENs) enabled determination of uptake and localization of both CENs and Ni²⁺ in the cell.

We find that NiCl₂ is most toxic, followed by Ni-SiO₂, hNi@SiO₂ and, lastly, nhNi@SiO₂. The toxicity ranking of the CENs correlates well with the intracellular Ni²⁺ concentration from CEN dissolution (Ni-SiO₂ > hNi@SiO₂ > nhNi@SiO₂). Interestingly, however, all CENs result in higher intracellular Ni²⁺ than NiCl₂, despite their lower toxicity. Ongoing confocal microscopy studies aim to demonstrate that Ni²⁺ from NiCl₂ diffuses into the cells and affects many cellular compartments, including the cytoplasm and nucleus. In contrast, CENs predominantly dissolve in the lysosome's acidic environment and Ni²⁺ hence remains localized, reducing toxicity.

Overall, our results indicate a Trojan horse mechanism, where the CENs facilitate transport into the cell, and dissolution within the cell rather than the Ni NPs themselves results in a toxic response. However, both localization of the CEN and their rate of dissolution further strongly affect CEN toxicity.

Thursday, August 18, 2016
Ecotoxicology & Bioavailability IV
2:30 PM

**Silver and gold accumulation by *Chlamydomonas reinhardtii*
after exposure to Three-Layered Silver Nanoparticles
(Ag@Au@Ag)**

Dominic Ponton, USGS

Dominic E. Ponton, Sahar Pourhoseini, Ruth C. Merrifield, Marie-Noëlle Croteau, Jamie R. Lead, Samuel N. Luoma, Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, Arnold School of Public Health, University of South Carolina, Columbia, 29208, SC, USA, United State Geological Survey, 345 Middlefield Rd, Menlo Park, 94025, CA, USA, University of California Davis, 1 Shields Ave, Davis, CA, USA, 95616

For silver nanoparticle (Ag NP) exposures, the role of the ions and particles in Ag bioaccumulation and toxicity has not been fully elucidated, with many reported studies suggesting that only Ag ions are taken up. We used an innovative tool, i.e., a three layered core-shell-shell Ag NPs (Ag@Au@Ag) to address the particle versus ion uptake question. The Ag core of these NPs was prevented from dissolution by a gold (Au) layer, while the outer Ag layer coated with polyvinylpyrrolidone (PVP) could dissolve. We exposed the green alga *Chlamydomonas reinhardtii* to a range of environmentally realistic Ag concentrations (1 to 50 nM) as Ag@Au@Ag NPs dispersed in moderately hard synthetic freshwater and traced Ag and Au in both algae and media. The proportion of dissolved Ag measured by centrifugal ultra-filtration varied from 4 to 16% at the beginning of the exposure and was higher at lower NP concentrations. Uptake rates of Ag and Au by algae increased with increasing NP concentrations. The uptake rate constant for Ag ($k_{uw} = 28 \pm 2$ L/g/min) was similar to that for Au (31 ± 2 L/g/min), suggesting NP uptake. In contrast, uptake rates for Ag from AgNO₃ increased linearly with Ag concentration, but begin to go non-linear at Ag concentrations greater than 10 nM. The k_{uw} for Ag⁺ was about 3.5 times lower (8.2 L/g/min) than that for the Ag@Au@Ag NPs. Ratio of Ag/Au in the medium before exposure was 2.6 ± 0.02 and increased to 2.96 ± 0.02 after exposure and was intermediate in *C. reinhardtii* (2.31 ± 0.11). These results suggest that both forms of Ag are taken by the alga *C. reinhardtii*. Next, transmission electronic microscopy will allow localizing the NPs with the algae.

Ecotoxicology and Bioavailability

Posters



Monday, August 15, 2016
Poster Session I
E-101

Combined toxicity of nanosilver and nanotitania: comparing light and dark conditions

Carolyn Wilke, Northwestern University
Jean-François Gaillard, Kimberly A. Gray

Estimates of current engineered nanomaterial (ENM) concentrations in the environment, as well as the forecasted trends in ENM utilization and predicted future releases, all point to the accumulation of complex ENM mixtures in the natural environment. However, ecotoxicological testing of ENMs thus far has focused on single nanomaterials and their environmental transformations. This environmental processing that transforms nanomaterials includes interaction with other ENMs and co-contaminants, which alters their morphological and chemical characteristics, as well as their toxicity to environmental organisms. Will complex environmental mixtures containing various ENMs lead to toxicological outcomes that are synergistic, attenuated, or simply additive? To investigate this question, we evaluated the chemistry and toxicity of nanosilver and nanotitania, which we selected based on their frequency of use, chemical properties, and likelihood of interacting. We tested their combined toxicity to *E. coli* bacteria using high throughput assays under both light and dark conditions in Lake Michigan water. Under dark conditions, we observe that at low concentrations of nanosilver, nanotitania is able to mitigate nanosilver's toxicity by adsorbing silver ions onto its surface. Under simulated solar irradiation, however, the combined effects of the two nanoparticles yield synergistic toxicity. In an effort to explain this synergistic interaction, we also studied the chemical interaction between these ENMs by measuring nanotitania's adsorptive capacity for silver ions and the production of reactive oxygen species under light for mixtures of nanosilver and nanotitania. We propose that under illumination the environmental processing of nanosilver and nanotitania mixtures produces a nanosilver/nanotitania hybrid material that self-assembles and acts through a combination of mechanisms to be more toxic than the sum of the components. Our results highlight the significance of interactions between ENMs in altering their environmental chemistry and moderating their ecotoxicity.

Monday, August 15, 2016
Poster Session I
E-102

Testing food grade and nano-TiO₂ on a defined human intestinal community

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Titanium dioxide is a white metal oxide, which is commonly used as a pigment in coatings of candies and chewing-gum. Food-grade TiO₂, referred to as E171 in Europe and INS171 in North America, includes a nano-sized fraction, representing up to 44% of the particles. Due to concerns about TiO₂ nanoparticles (NPs) as potentially hazardous, at least by inhalation, the toxicity of ingested TiO₂ NPs are currently under investigation. However, the impact of confectionary titania have yet to be determined. We used a defined gut bacterial community, MET-1 (microbial ecosystem therapeutic-1), as a model human intestinal community. The anaerobic consortium containing 33 bacterial species was batch cultured (n=30) for 48 h at 37°C in a starch-based medium. Food-grade TiO₂ from several suppliers were used to amend the cultures at two realistic concentrations (based on a single unit of gum; 100-250 ppm). In addition, purchased TiO₂ NPs (25 nm; P25) were used. The impact of the additives was assessed with physiological, biochemical and molecular assays. Gas production was monitored using gas chromatography, and fatty acid methyl ester (FAME) analysis used the MIDI Sherlock Microbial Identification System protocol. DNA analysis included polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE) and 16S ribosomal RNA gene fragment 454-pyrosequencing. Our results showed that TiO₂ particles had no impact on gas production nor on fatty acid composition. Only a food grade sample (n°1) induced a small variation in culture gas composition, when tested at 250 ppm (p<.05) and this, as well as P25 particle controls, resulted in a limited shift in the saturated fatty acid composition (12:00 and 14:00, p<.05). PCR-DGGE profiles and phylogenetic distributions obtained from 454 pyrotag 16S rRNA gene sequencing confirmed a modest impact on the bacterial community (food grade n°1 and P25), with a significant decrease in sequences corresponding to the dominant *Bacteroides ovatus* (-10%) in favor of *Clostridium. cocleatum* (+10%; p<0.05). Despite these minor shifts in the relative abundance of two members of the model gut consortium, taken together, we believe that food grade titania and TiO₂ NPs particles do not have a major impact on the human gut microbiota when tested at realistic concentrations.

Monday, August 15, 2016
Poster Session I
E-103

Evaluation of nanoreprotoxicity and steroidogenic responses induced by ZnO nanoparticles and bulk ZnO in mouse testis Leydig cells TM3 in vitro

Gautam Kaul, ICAR-NDRI University
Nisha Bara

Zinc oxide nanoparticle (ZnO NPs) is one of the most important nanomaterial with widespread applications. The current study was to evaluate the direct effect of ZnO NPs on steroidogenesis, by taking mouse testicular leydig cells (TM3) as in vitro model. In addition, we also evaluated the uptake, intracellular behaviour, cytotoxicity, morphological changes of ZnO NPs at different concentrations (0-200 µg/mL) in TM3 cells and compared them with their respective bulk form. Concentration and time dependent cytotoxicity and morphological changes were regularly and prominently observed for ZnO NPs. A significant decrease in TM3 cell viability started at 2 µg/mL concentration of ZnO NPs even at 1 h incubation. ZnO NPs were found to increase the antioxidant enzymes activity, SOD and CAT. Apoptosis was increased after 4 h exposure. TEM micrographs indicated that ZnO NPs was uptaken by leydig cells, resulting in autophagosomes, autolysosomes, and autophagic vacuoles formation. Real time data indicated that in TM3 cells, ZnO NPs significantly increased the steroidogenesis related genes (StAR and P450scc) and decreased the SOD, an antioxidant enzyme gene expression, after 4 h incubation, while 12 h incubation could not change the expression pattern of these genes. Moreover, ZnO NPs exposure significantly increased the testosterone production at 2 µg/mL concentration after 12 h incubation. In conclusion our finding demonstrated that ZnO NPs are highly cytotoxic, enhancing apoptosis, autophagic vacuoles formation, morphological changes, and alteration in antioxidant enzymes activity in TM3 cells. Moreover, our finding also demonstrated that ZnO NPs are causing steroidogenic effect in leydig cells, which is highly dependent on exposure time and concentration.

Monday, August 15, 2016
Poster Session I
E-104

Assessing the Environmental Impact of Nanoparticles and Evaluating a Redesign Strategy

Joseph Buchman, University of Minnesota

Due to their novel properties, engineered nanoparticles are produced at a large scale for use in consumer products. With such widespread use, it is inevitable that engineered nanoparticles will be released into the environment. The fate of nanoparticles after they enter the environment and their impact on organisms are not well understood. To address this deficiency, this study explores the effects of nanoparticles to bacterial models which, being at a low trophic level, serve as a good diagnostic for overall environmental health. Polyallylamine hydrochloride (PAH)-functionalized gold nanoparticles have shown varying toxicity to and association with different bacterial strains. Generally, nanoparticles do not get internalized by healthy gram-negative bacteria, but instead adsorb to their surface; as such, in this work, an important surface structure of gram-negative bacteria called lipopolysaccharides (LPS) has been hypothesized to be a critical mediator of nanoparticle/bacteria interactions. The collected data show that *S. oneidensis* MR-1, a bacterium known to present rough LPS, was the most resistant to PAH-functionalized gold nanoparticles while *A. vinelandii* UW and *P. aeruginosa* PAO1, which have smooth LPS, were sensitive to PAH-functionalized gold nanoparticles. In parallel experiments, another engineered nanomaterial, iron oxide nanoparticles, was coated with a mesoporous silica coating as a strategy for reducing their effects on bacteria. In fact, this coating does mitigate the effects of the iron oxide nanoparticles to the bacteria. Also, the mesoporous silica shell leads to reduced association between the iron oxide nanoparticles and the bacterial membranes. Since the mesoporous silica coating ameliorates the iron oxide nanoparticle effects on bacteria, it may be a viable redesign strategy for reducing nanoparticle impacts on bacteria in the environment.

Monday, August 15, 2016
Poster Session I
E-105

Transformation and behavior of silver nano-particles in contact with algal cells - how they influence toxicity?

Anzhela Malysheva, University of South Australia
University of Copenhagen

As suggested by OECD guidelines for environmental risk assessment of manufactured nanomaterials, NPs are to be characterized and their concentrations measured - throughout the test duration - to account for transformations and possible losses, and correctly estimate the exposure dose. This information is also necessary to link specific characteristics of NPs to observed negative effects, and look into the mechanisms of toxicity. To link the variability of described processes with characteristics of NPs, we used a library of 9 Ag NPs of various surface functionality and size, and chose algal growth inhibition test as from the OECD guideline for aquatic toxicology. Many techniques are currently available for nano-characterization, including high resolution microscopy techniques, classic light scattering methods, and nano-specific elemental analyzers. We relied on time resolved ICP-MS to measure NP concentration, size distribution and aggregation state in test suspensions and, for the first time, in the presence of exposed organisms. This method has been a groundbreaking tool for characterization of NPs in environmental matrices, but has hardly seen any use in toxicological studies. Finally, with the aid of conventional ICP-MS we performed measurements for a complete mass distribution of silver in the test systems, distinguishing dissolved fraction from nanoparticulate by ultrafiltration; particles in suspension from adsorbed on the container wall by adsorption test; particles associated with the cell surface from those internalized by chemical etching. As a complementary technique, we used dark field microscopy to image Ag NPs with different surface coatings associated with cells after 24h of exposure.

The primary objectives of this study were: 1) to assess the dissolution, aggregation of Ag NPs and their sorption to the container walls in presence of algal cells; 2) to investigate interactions between cells and Ag NPs and distinguish surface interactions from cell internalization; 3) to interpret the results of algal growth inhibition assay considering the measured concentrations, occurred transformations, and the cellular uptake.

Monday, August 15, 2016
Poster Session I
E-106

New insights into mechanisms underlying silver nanoparticle-directed mast cell activation

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Jared M. Brown (Skaggs School of Pharmacy and Pharmaceutical Sciences,
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Nanoparticle-mediated toxicity often involves triggering immune responses that includes mast cell activation. Mast cells are effector cells that can regulate both innate and adaptive immune responses. Silver nanoparticles (AgNPs) are one of the most prevalent nanomaterials used in consumer products due to their antimicrobial/antifungal properties. We utilize bone marrow-derived mast cell (BMMC) isolated from C57Bl/6 mice. Previously, we have shown that AgNPs induce mast cell degranulation and we identified a role for scavenger receptor B1 (SR-B1) in AgNP-directed mast cell degranulation. However, it is completely unknown how SR-B1 mediates mast cell degranulation and the intracellular signaling pathways involved. We hypothesized that SR-B1 interaction with AgNPs directs mast cell degranulation through activation of upstream calcium signaling that involve phosphoinositide 3-kinase (PI3K) and phospholipase C γ (PLC γ) and subsequent influx of extracellular calcium through the ORAI calcium channels. Our results demonstrate that AgNP-mediated mast cell degranulation is dependent on an influx of extracellular calcium, which appears to be at least partially mediated by the ORAI1 calcium channels. Moreover, we found that both PI3K and PLC γ are involved in degranulation of mast cells in response to AgNPs. Taken together, our results provide new insights into AgNP-induced mast cell degranulation, which could be beneficial for designing novel nanomaterials that are devoid of immune system activation.

Monday, August 15, 2016
Poster Session I
E-107

Determining Phytotoxicity of Carbon Nanotubes in Heat Stressed Crops

Juliette Jordan, The Institute of Environmental and Human Health. Texas Tech University

Jaclyn E. Canas-Carrell- Department of Environmental Toxicology, The Institute of Environmental and Human Health. Texas Tech University, Lubbock, Texas, Paxton Payton â USDA-ARS Cropping Systems Research Laboratory, Lubbock, Texas, David Tissue â Hawkesbury Institute for the Environment, Western Sydney University, Australia

Climate change, which is currently of great concern to the science community and general public, may lead to dramatic changes in weather patterns. These changes dictate a better understanding of how ecosystems might be affected, including effects on crop growth as well as the fate and toxicity of contaminants. Carbon nanotubes (CNTs) are currently used in a wide-range of commercial and agricultural applications. The increasing use of CNTs in fertilizer, pesticide, and herbicide delivery systems could have direct, unintended consequences on soil health, the microbiome, and managed and native ecosystems. Limited studies have examined the impact of CNTs on abiotic stress response and potential consequences on plant CNT uptake with respect to plant performance and subsequent potential human exposure to CNTs. In this study, the effect of CNTs in soil on plant performance under periodic thermal stress (heat waves) was examined. Cotton and tomato were grown in soil !

spiked with multi-walled carbon nanotubes (MWCNTs) (100 mg/kg soil) under two temperature regimes with natural lighting: 1) Control T = 28/18°C day/night and 2) Elevated T = 32/22°C day/night. The impact of elevated growth temperature and the interaction with MWCNTs on water use efficiency (WUE) was measured, along with the impact of periodic heat waves on photosynthesis. Preliminary analysis of this data indicates that the presence of MWCNTs in soil significantly decreased WUE in cotton but not in tomato. We found that MWCNT exposure to cotton plants under heat stress had a negative effect on plant growth and photosynthetic rate. These results may add a new variable to the equation for CNTs effect on plants. Past studies have shown that results vary depending upon plant species and CNT type. Climate may exacerbate the impact of CNTs on plant growth. A complete analysis of these results will be presented.

Monday, August 15, 2016
Poster Session I
E-108

Dynamic Monitoring of Cytotoxicity of Nanoscale III-V Particulates and CMP Nanoparticles

Chao Zeng, University of Arizona
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Alvarez

III-V semiconductor materials such as gallium arsenide (GaAs) and indium arsenide (InAs) are increasingly used in electronic devices. During semiconductor manufacturing, III-V films are subjected to chemical mechanical planarization (CMP) to create a highly planar surface. CMP processes utilize slurries containing abrasive nanoparticles (NPs) including silica (SiO₂), ceria (CeO₂) and alumina (Al₂O₃) to facilitate the removal of excess materials from III-V films. CMP processes, which are characterized by a high water demand, can generate high volumes of effluents containing inorganic oxide NPs as well as nanoscale III-V particulates. Therefore, it is important to understand the potential risks from these NPs to human health and natural environment.

In our study, the cytotoxicity of nano-sized GaAs, nano-sized InAs and inorganic oxide NPs in model CMP slurries towards 16HBE14o- human bronchial epithelial cells was evaluated using a novel label-free real time cell analyzer (RTCA). RTCA monitors cell proliferation and viability through impedance detection. In this assay, cells are seeded in plates contain microelectronic sensor arrays and the interaction of cells with the sensors generates an impedance response. Cell biological status including cell number, morphology, adhesion, viability will all affect the measurement of impedance that is expressed by cell index. RTCA system allows dynamic measurement and calculation of time-dependent IC₅₀ values.

Our results demonstrated that III-V NPs are toxic to 16HBE14o- cells. Although GaAs and InAs NPs generated similar characteristic kinetic patterns, GaAs displayed much higher toxicity (IC₅₀ - 2.0 mg/L) than InAs (IC₅₀ - 30 mg/L). We found cytotoxicity from these NPs was mainly caused by the dissolution of highly toxic arsenic. For example, 24.1 and 3.9 mg/L of As were released into the medium in the bioassays supplied with 250 mg/L GaAs and InAs NP after 24 h of exposure. Colloidal SiO₂ was the only slurry that was cytotoxic within the concentration range tested, albeit at relatively high concentrations. Exposure to 125 mg/L SiO₂ resulted in cell cycle arrest; at 625 mg SiO₂/L cell detachment was observed immediately after its introduction. Finally, we found these nanomaterials can also affect cell signaling and reduce cell response to ATP. These results indicate that the release nanoscale GaAs, InAs particulates in CMP effluents should be controlled to the hazardous potential to humans and the environment.

Monday, August 15, 2016
Poster Session I
E-109

Are Zebrafish Hatching Assays Suitable for High-Throughput Screening?

Sharlee Mahoney, University of Pittsburgh
Jason Ferree, Qing Bai, Edward A. Burton and Goetz Vesper

The rapid spread of functional nanomaterials in industrial application and consumer products motivates the search for facile, sensitive, rapid, and robust high-throughput nanotoxicity screening assays. Zebrafish (*Danio rerio*) is emerging as a well-suited *in vivo* model for nanotoxicity studies due to prolific breeding, embryo tissue transparency, rapid development time, and the relative simplicity of controlled toxin exposure. Zebrafish allows the use of diverse assays including hatching, survival, and malformations. Among those, hatching is widely used due to its simplicity, speed, and ability to be conducted in multi-well plates. Hence, it seems well-suited for high-throughput nanomaterial toxicity screenings.

In the present work, we evaluated zebrafish hatching assays for nanotoxicity studies of Ni/SiO₂ complex engineered nanomaterials (CEN). We synthesized and characterized three nanomaterials that mimic widely used industrial CEN: Ni nanoparticles deposited on silica supports, embedded in porous silica, and encapsulated in hollow silica shells. Their toxicity was tested using a high-throughput approach prevalent in the literature: one zebrafish was placed in a well of a 96-well plate and hatching rate was monitored vs time. Surprisingly and counter to other assays conducted in parallel- only one of the three nanomaterials appeared toxic and inhibited hatching compared to the control. However, we also observed slightly delayed hatching of the control zebrafish, presumably due to accumulation of excreted metabolites (ammonia) in the small media volume per well. Indeed, transition to a higher volume:fish ratio in a 12-well plate removed this delay and revealed toxicity for all three nanomaterials. These results suggest an interesting interaction between the toxicity of metabolites and that of Ni: We hypothesize that the formation of a Ni(NH₃)₆²⁺ complex caused mutual mitigation of the two toxins. This was confirmed in *ex-situ* experiments by monitoring the free ammonia concentration upon Ni²⁺ addition, confirming a drastic decrease in free ammonia concentration with the addition of small Ni²⁺ concentrations.

Overall, our results represent an interesting case where interactions between two different toxins result in mutual mitigation. This suggests that great care must be taken when using high-throughput hatching assays since unexpected interactions between zebrafish metabolites and nanomaterials could result in spurious, if not wrong, toxicity reports.

Monday, August 15, 2016
Poster Session I
E-110

The Interactive Effects of UV Radiation and Titanium Dioxide Nanoparticles on the Calanoid Copepod, *Acartia tonsa*

Vena Haynes, University of Connecticut
J. Evan Ward, University of Connecticut

Titanium dioxide nanoparticles (TiO₂ NP) are used in a variety of consumer goods including paints, sunscreens, skin-care products and anti-microbial agents. As a result of their prevalent use, especially related to beach and boating activities, TiO₂ NP are likely entering the marine environment via direct and indirect inputs. Nanoscale TiO₂ NP are photocatalysts, able to produce reactive oxygen species (ROS) that can damage living cells and cause deleterious effects in some aquatic organisms. This study investigated the effects of commercially available TiO₂ NP on the female calanoid copepod, *Acartia tonsa*. Four experimental treatments, a) copepods with NP and food, b) copepods with food only, c) NP with food and d) food only, were exposed to three different light conditions (15-hr light, 9-hr light and 0-hr light as a control). Light was supplied by solar lamps that mimic natural light in the visible and UVA/B regions. An oceanographic optical model, Hydrolight, was used to determine the appropriate environmental light levels for experiments. Initial and final algae concentrations were determined to evaluate the effects on copepod ingestion rate (IR). Egg production rate (EPR) was determined after 24 hours of exposure, and egg hatching frequency (HF) was determined at 48 hours. Preliminary results indicate that there is both NP and light effects on copepod IR, EPR and HF, compared to the NP and 0-hr light controls. These and other effects will be presented. This work suggests that NP under realistic environmental conditions could have possible organismal and population impacts, and will help to inform future studies on organisms that rely on zooplankton for food (e.g., fish larvae and filter-feeders).

Monday, August 15, 2016
Poster Session I
E-111

Soil microbial communities and soil function in response to metal oxide engineered nanomaterials involved in energy storage technologies

Helena Avila-Arias, Purdue University

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Along with the growing human population, increasing demand on energy and developing economies worldwide, energy storage represents a challenge; power the myriad of portable electronic devices and electric/hybrid electric vehicles, and storage of electricity produced by renewable energy technologies. Metal oxide engineered nanomaterials (MO-ENMs), including nano molybdenum oxide (nanoMoO₃), nano nickel oxide (nanoNiO) and nano lithium oxide (nanoLi₂O), have wide application in energy storage and emerging fuel cell technologies. Production and application of ENMs will lead to inevitable environmental release during all life cycle phases; manufacturing, delivery, use, and/or disposal. Environmental concentrations of most ENMs are unknown, but exposure modeling studies suggest soil as the major sink of ENMs released to the environment. This is the first study to assess soil response to nano MoO₃, nanoNiO, and nanoLi₂O. During 60 days, we evaluated the effect of these MO-ENMs on greenhouse gas (N₂O, CH₄, and CO₂) emissions (GHG), soil enzyme (β -glucosidase and urease) activities, and microbial communities (bacterial, archaeal and eukaryal) in soil microcosms under MO-ENMs pollution at three different concentration levels (low, medium and high). No clear pattern was observed of GHG in soils exposed to nanoMoO₃ and nanoNiO. We observed an effect on β -glucosidase activity in soil under nanoMoO₃ and nanoNiO presence. However, this was further reversed. Soil under nanoLi₂O at 458 μ g Li/g soil affected GHG, where CH₄ and CO₂ emissions were both significantly higher with respect to the control. Also, both enzyme activities were affected; β -glucosidase decreased while urease activity increased. All MO-ENMs shifted the three domains of microbial community structures at increasing metal concentrations, except by archaea community under nanoLi₂O presence. It still remains unknown what kind of microorganisms and metabolic potential are affected by these MO-ENMs, which our future efforts will focus on. By identifying this, we will understand the effect of nanoMoO₃, nanoNiO and nanoLi₂O in soil systems and, in the bigger picture, move forward the knowledge in the field of soil resilience from a microbial ecology point of view. Are there any microbial species and metabolic function essential for the stability, activity and resilience of the system?

Monday, August 15, 2016
Poster Session I
E-112

Uptake of Nanoparticles by Fresh Water Algae using Single Cell ICP-MS

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Dr Jamie Lead (Center for Environmental Nanoscience and Risk, University South Carolina, SC, USA) and Dr Chady Stephan (Perkin Elmer, Shelton, CT)

Single cell-ICP-MS is an emerging technology allowing users to; monitor metal content within single cells, measure the intrinsic metal content of cells, measure uptake of both ionic and nanoparticulate metal contaminants, handle low cell numbers compared to conventional methods and requires minimal sample preparation.

Tuesday, August 16, 2016
Poster Session II
E-201

Microbial Toxicity of Cadmium Telluride Quantum Dots Towards Escherichia coli K-12 (Guyer)

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Joanne Vassallo, Rich Boden, and Richard D. Handy (School of Biological Sciences, Plymouth University, UK).

Quantum dots consist of semiconductor nano-sized particles, with an outer coating layer determining their stability and/or biological design requirements. Industrial-scale production of nanomaterials raises concerns about novel or unforeseen properties. The minimum inhibition concentration assay was used to screen cadmium telluride quantum dots (CdTeQD) having a carboxylate, ammonium or polyethylene glycol (PEG) coating against Escherichia coli K12 (Guyer). The toxicity was compared to that of bulk CdTe and cadmium chloride. Actively growing cultures (basal medium with 10mM glucose as sole carbon and energy source) were exposed to a dilution series of the test suspensions in 96-well plates (n = 6 plates/treatment). A test suspension exposure, at identified sub-lethal concentrations, followed in Erlenmeyer flasks (n = 3 flasks/treatment). The magnitude of growth inhibition was chosen as the end-point. The amount of glucose remaining after each exposure was measured. For all test suspensions, nanoparticle tracking analysis revealed natural particle aggregation and dialysis experiments showed minimal dissolution of cadmium and tellurium at pH 6.5. Complete microbial growth inhibition was recorded at 6 mg/L for the ammonium-coated, 25 mg/L for the carboxylate-coated and 100 mg/L for the PEG-coated CdTeQD. CdTe bulk and cadmium chloride were not found to be toxic to the microbe. The size of the quantum dots may be an important factor that determines their toxic effect, irrespective of the physico-chemical properties of the exposure medium. On-going work is assessing glucose metabolism and the resulting carbon yields from the sub-lethal concentration exposures of nanomaterials.

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E-202

Effects of TiO₂ nanoparticles on oyster hemocytes: in vitro studies under light and dark conditions.

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In marine molluscs, physiological responses to environmental stresses are mediated, in part, by hemocytes that are found in the open circulatory system. These cells are critical for the innate immune response and act to recognize, phagocytize, and oxidize nonself particles. The purpose of this study was to examine the immunological response of oyster hemocytes (*Crassostrea virginica*) following exposure to bulk (>1 μm) and nanoparticulate (<90 nm) titanium dioxide (TiO₂). Two different types of nanoparticles (NP), both commonly found in consumer products, were used in the experiments: 1) UV-Titan M212 (93% rutile) and 2) 100% anatase form. Hemolymph was withdrawn from the adductor muscle of oysters and exposed to the aforementioned particles at concentrations of 0.1, 0.5 and 1.0 mg/L, for two and four hour periods under both dark and environmentally-relevant light conditions (350-800 nm). At the end of the incubation period, the mortality, phagocytosis, and oxidative stress of hemocytes were evaluated using flow-cytometric assays. Results indicated that under dark and light conditions, exposure to bulk or NP TiO₂ had minimal apparent effects on oyster hemocytes. Under some experimental conditions, NP caused significant changes in phagocytosis under both dark and light conditions, compared to hemocytes exposed to larger 'bulk' particles and un-exposed control hemocytes. Photoactivation of TiO₂ did not enhance the effects of NP. Findings of this work demonstrate that oyster hemocytes are relatively insensitive to TiO₂ NP following acute, in vitro exposures of up to 4 hours under dark and light conditions.

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E-203

Effects of Salinity on Toxicity of Water- Dispersible, Single-Walled Carbon Nanotubes to Japanese Medaka Eggs

Shosaku Kashiwada, Toyo University

Since concern has arisen about the environmental hazards and risks posed by nanomaterials, there have been many toxicological investigations of carbon and metal nanomaterials. Carbon nanotubes (CNTs) are among the most industrially important nanomaterials and are therefore generating environmental concern. Nanomaterials readily aggregate in solution, and even more so in saltwater. Salinity is an important aquatic environmental determinant of the behavior and fate of chemicals, as are pH and temperature. Most aggregated nanomaterials are no longer nano-sized; instead, they are micron-sized in all dimensions. Generally, it is more difficult for these bigger materials to pass through biological membranes. Salinity also has other interesting effects on the behavior and bioavailability of nanomaterials. To investigate the effects of salinity on the behaviour and embryonic fish toxicity of functionalized, single-walled carbon nanotubes (SWCNTs), medaka eggs were exposed to non-functionalized single-walled carbon nanotubes (N-SWCNTs), water-dispersible, cationic, plastic-polymer-coated, single-walled carbon nanotubes (W-SWCNTs), or hydrophobic polyethylene glycol functionalized, single-walled carbon nanotubes (PEG-SWCNTs) at different salinities, from freshwater to seawater. As reference nanomaterials we tested dispersible chitin nanofiber (CNF), chitosan-chitin nanofiber (CCNF), and chitin nanocrystal (CNC, i.e. shortened CNF). Under freshwater conditions, with exposure to 10 mg/l W-SWCNTs, the yolk sacks of 57.8% of eggs burst, and the remaining embryos had reduced heart rate, eye diameter, and hatching rate. Hatched larvae had severe defects of the spinal cord, membranous fin, and tail formation. These toxic effects increased with increasing salinity. Survival rates declined with increasing salinity and reached 0.0% in seawater. In scanning electron microscope images, W-SWCNTs, CNF, CCNF, and CNC were adsorbed densely over the egg chorion surface; however, because of chitin's biologically harmless properties, only W-SWCNTs had toxic effects on the medaka eggs. No toxicity was observed from N-SWCNT and PEG-SWCNT exposure. We demonstrated that water dispersibility, surface chemistry, biomedical properties, and salinity were important factors in assessing the aquatic toxicity of nanomaterials.

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E-204

The effect of Nanoparticle Abrasives in Chemical Mechanical Planarization Slurries on Morbidity and Body Size of *Daphnia magna*

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The purpose of this study was to determine the acute toxicity to *Daphnia magna* (*D. magna*) of the nanoparticle (NP) component of chemical mechanical planarization (CMP) slurries. The semiconductor manufacturing industry uses metal oxide NPs such as colloidal silica (c-SiO₂), fumed silica (f-SiO₂), ceria (CeO₂), and alumina (Al₂O₃) as abrasives in CMP processes to polish wafer surfaces to high tolerances. While the semiconductor industry is interested to understand the potential ecological risks associated with the NPs contained in these slurries, assessing the toxicity of real-world CMP slurries is problematic due to the toxic constituents they are known to contain. In response to this challenge, a major CMP slurry manufacturer has produced model slurries of c-SiO₂, f-SiO₂, CeO₂, and Al₂O₃ that do not contain toxic additives, thus focusing the assessment on the metal oxide NPs themselves. Herein, we present the acute toxicity to *D. magna* of these four model CMP slurries, which have been thoroughly characterized by a toxicity consortium of the Semiconductor Research Corporation (SRC). *D. magna* is a fresh water flea known to be sensitive to ecological pollutants and is recommended by the Environmental Protection Agency (EPA) for ecotoxicity tests. *D. magna* neonates (less than 24-h old) were exposed to model CMP slurries at various concentrations for 96 h. Morbidity was recorded at 24-h intervals and the sizes of the surviving daphnia were measured at 96 h. The c-SiO₂ CMP slurry (up to 4 mg/mL) and the f-SiO₂ CMP slurry (up to 5 mg/mL) were not toxic to *D. magna* and did not reduce body sizes. The CeO₂ CMP slurry showed no morbidity up to 2 mg/mL; however, *D. magna* body sizes decreased as a function of the CeO₂ NP concentration. The Al₂O₃ CMP slurry was the only one among the four slurries that showed acute lethal toxicity to *D. magna* with a 96-h LC-50 of 1.1 ± 0.2 mg/mL. Moreover the body sizes of *D. magna* exposed to 1.5 mg/mL of Al₂O₃ CMP NPs decreased by nearly 53%. Overall, the results demonstrate that different pristine model CMP NPs exert different acute toxic effects on *D. magna* morbidity or growth, or both.

Copper and silver nanoparticles effects in *Danio rerio* embryos

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Metal nanoparticles (NPs), including silver (Ag) and copper (Cu), were increasingly manufactured in the last decades. Both Ag and CuO NPs possess antimicrobial properties and are being increasingly incorporated into consumer goods. This industrial proliferation and ensuing discharges could lead to accumulation in aquatic environments. Although surface waters are predicted to receive low levels of NPs, deleterious effects could occur in aquatic organisms. This study aims to assess and compare the effects of Ag and copper oxide (CuO) NPs in zebrafish (*Danio rerio*) embryos. To determine acute toxic concentrations, *D. rerio* embryos were exposed to Ag and CuO NPs (<100 nm) and ionic Ag and Cu [as silver nitrate (AgNO₃) and (CuSO₄); reference materials] for 96h (following OECD guideline TG236). Suspensions were refreshed every 24h. Nanoparticle tracking analysis (Nanosight) and dissolution analysis (ICP-MS) were performed in test solutions to evaluate behavior of NPs. Dissolution of Ag and CuO NPs was 2% ($93 \pm 7 \mu\text{g/L}$) and 0.4% ($524 \pm 51 \mu\text{g/L}$), respectively. CuO and Ag NPs smaller than 70 nm were most abundant. After 24 h, larger agglomerates (~ 150 nm) of CuO NPs had decreased substantially from the water column (4-fold) while Ag NPs maintained their dispersity. Metal analysis shows a steady decayed (6-fold) of Cu and stability of Ag concentration during 24h, suggesting sedimentation of CuO NPs and aggregation of Ag NPs. Ag and CuO NPs inhibited 50% hatching of zebrafish embryos at 6 and 3 mg/L, respectively, at 96 h. Moreover, CuO NPs-exposed embryos had a coating of NPs in the chorion. Data suggests that dissolved Cu²⁺ mediated the inhibition of ZHE (zebrafish hatching enzyme), which is released into the chorionic fluid. Metal analysis in exposed embryos showed that high concentrations of NPs was associated with the chorion ($5797 \pm 962 \text{ ng Cu/embryo}$ and $143 \pm 37 \text{ ng Ag/embryo}$ in chorionated embryos), but did not accumulate in the embryo tissues ($453 \pm 69 \text{ ng Cu/embryo}$ and $0.3 \pm 0.04 \text{ ng Ag/embryo}$ in dechorionated embryos) to the same extent. Sub-lethal exposures showed a significant and similar depletion of total glutathione in embryos exposed to Ag and Cu (both NPs and ionic reference materials), but still insufficient to induce superoxide dismutase activity that remained similar among Ag and Cu treatments. Sodium/potassium ATPase activity only showed a significant reduction in embryos exposed to ionic Ag. This study contributes to the portrayal of the mechanisms of action of Ag and CuO NPs in zebrafish embryos.

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Mechanisms for toxicity of a next generation energy storage nanomaterial to *Daphnia magna*

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While precedent studies have investigated the behavior of simple metal oxides, emerging technologies such as energy storage are utilizing more complex and multi-component nanoscale metal oxides consisting of layered structures and redox-active metals. First generation materials such as lithium cobalt oxide (LCO) are being replaced by next generation nanomaterials such as lithium nickel manganese cobalt oxide (NMC). Next generation electric vehicles are predicted to utilize more than 100 kg of nanoscale Li-NMC per vehicle as a battery cathode material, leading to many potential exposure scenarios. In this study, we are comparing LCO to NMC with varying amounts of cobalt, nickel and manganese as a model system for assessing the potential environmental impact of nanomaterials for energy storage on the environmentally relevant aquatic invertebrate, *Daphnia magna*. The impacts of these particles on *D. magna* were determined in acute and chronic assays, measuring end points in body size, reproduction and mortality. Acute studies demonstrate no effect on daphnid mortality up to 25 mg/L whereas chronic studies show significant impacts to daphnid reproduction at the lowest concentration tested, 0.1 mg/L. Additionally, toxicity from metal dissolution was accounted for and showed no affect, leading us to believe that this is a nanomaterial-specific impact either through direct contact and localization of metal ions. Lastly, our study investigated gene expression. Results indicate a nanomaterial specific down regulation of a number of important genes potentially indicating that daphnids metabolism are shutting down. This study shows that we may be able to mitigate negative biological impacts by altering battery material chemical composition.

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Nanotoxicology of NMC and *D. melanogaster*

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Investigations of the potential environmental impacts of nanoparticles have largely focused on model or simple nanomaterials. The current work exposes *Drosophila melanogaster* to Lithium Nickel Manganese Cobalt Oxide (NMC), a complex next-generation battery material. In initial trials, no significant mortality was observed in *D. melanogaster* larvae exposed to NMC nanoparticles at 1, 10, 20 or 100 mg/L, utilizing two different methods: nanoparticle-treated food media and nanoparticle-treated aqueous sucrose solution. Existing studies commonly expose larvae to nanoparticles via mixture with food media, which introduces additional variables that may affect outcomes. Nanoparticles are less stable when introduced to food media, and homogenous mixing is difficult; methods described in existing research are often vague, e.g. nanoparticles were "mixed strongly" into the food media. Less commonly encountered in existing research is the method of exposing larvae via aqueous solution. The current work aims to standardize an aqueous larval oral exposure method and represents the first steps towards evaluating potential toxic effects of battery-related nanoparticles on *Drosophila melanogaster*. *Drosophila melanogaster*, due to its mapped, highly tractable genome, high percentage of homologous disease genes to humans, and a short ~10 day life cycle, is an exceptional model for examining potential toxic effects of exposure to NMC. Results seen in *D. melanogaster* will be used to compare impacts across various model organisms.

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E-208

Investigating Multigenerational Effects of Silver Nanoparticles in *Caenorhabditis elegans*: A Toxicogenomic Approach

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Studies in a nematode *Caenorhabditis elegans* have shown that exposure to pristine as-synthesized and sulfidized silver nanoparticles (sAg-NPs) can cause various toxic effects, but genomic effects that can be induced by prolonged exposure over multiple generations have not been investigated. A previous multigenerational study of continuous exposure of *C. elegans* to Ag-NPs and sAg-NPs also resulted in increased sensitivity in terms of reproductive toxicity with increasing number of generations exposed. This suggested that Ag-NPs may cause mutations or epi-mutations. In this study, we used wild type N2 *C. elegans* as a model organism to determine if mutations contribute to the observed multigenerational effects. Exposure was carried out using sub-lethal concentrations (EC30 for reproduction) of AgNO₃, Ag-NPs and sAg-NPs in simulated soil pore water for 10 generations with the parent generation (F0) unexposed for all groups. Six replicates were used per treatment, four of which were used to extract DNA from an entire brood for the whole genome DNA sequencing by NextSeq, and two for selecting individual worms for microsatellite instability analysis. So far, for four microsatellite loci analyzed, microsatellite mutations have not been observed for the wild type nematode. The sequencing data will also be aligned to the reference genome and comparisons within (from F0 to F10) and among treatments will be made to test whether exposure to Ag-NPs can induce mutations such as single nucleotide polymorphisms (SNPs), insertion and deletions and result in germline instability. Lack of microsatellite mutations in wild type *C. elegans* may be due to the presence of mismatch repair enzymes that are capable of repairing insertion/deletion mutations at microsatellite loci. To test this hypothesis, a mismatch repair mutant strain (*msh-2*) was exposed to pristine Ag-NPs at an EC30 for reproduction. The F0 generation was unexposed while F1 to F4 generations were exposed. Out of the two analyzed microsatellite loci, mutations were observed for one locus with mutation rate slightly increasing over four generations from 1.04×10^{-2} in controls to 4.17×10^{-2} after exposure to pristine Ag-NPs. The nature of mutations differed between controls (deletions) and exposed (insertions). Analyses of more microsatellite loci are ongoing to determine if more mutations occurred upon exposure at different microsatellite loci.

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The role of chorion on biological effects of metal oxide nanoparticles in zebrafish embryos

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The zebrafish embryo is surrounded by an acellular envelope known as chorion (1.5-2.5 μ thickness) that is composed of four major polypeptides with three layers. One of the major functions of chorion is to protect the embryo from exposure to inorganic chemicals such as metals and nanomaterials. Thus, it is possible to generate false negative nano-toxicity results due to a limited permeability of the chorion. In previous study, we found optimal dechorionating method using enzyme treatment (pronase, protease from *Streptomyces griseus*) and confirmed that enzyme treatment (pronase) doesn't affect physiological effects on zebrafish embryo. Enzyme-supported dechoriation was carried out as follows: Dechoriation with pronase treatment was performed in 24 hpf embryos. Embryos were incubated with 1 mg/ml pronase for 20 minutes and then rinsed at least 3 times to remove excess pronase. The objective of this study was to investigate the differences of biological effects among metal oxide nanoparticles (MO-NPs) in normal (with chorion) and dechorionated zebrafish embryos. Zebrafish embryos were exposed to MO-NPs for 96 h. The MO-NPs used in this study were CeO₂NP, CuONP, SiO₂NP, TiO₂NP, and ZnONP. Biological effects were observed on survival, heartbeat, and total length. As a result, normal and dechorionated zebrafish embryos exposed to CeO₂NP, SiO₂NP, and TiO₂NP were not significantly affected. However, survival and heartbeat were influenced by the presence/absence of chorion in zebrafish embryos exposed to ZnONP and CuONP. These results indicate that chorion could be an important factor that interrupts evaluating toxicity of certain types of NPs precisely and thus mislead the hazards/risk to human and ecosystem. Survival and heartbeat were influenced by the presence/absence of chorion in zebrafish embryos exposed to ZnONP and CuONP. We consider that ion released by MO-NPs was identified as important factor determining the MO-NPs toxicity. Thus we plan to find out whether differences of toxicity by the presence/absence of chorion in zebrafish embryos exposed to ZnONP and CuONP are due to metal ions. This study will help to develop a toxicological methodology using dechorionated zebrafish embryos from the perspective of regulation.

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E-210

Influence of sunlight on cerium oxide mediated nanoparticle toxicity in Cardinal tetras

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Most current nanotoxicological studies focus on only a few key model species, such as zebrafish, goldfish and trout. However, the knowledge of the impact of NPs on other aquatic system is very limited. Cardinal tetras are a common aquarium freshwater fish found the Rio Negro in the Brazilian Amazon. The Rio Negro has extremely low ion concentrations ($\sim 10 \mu\text{M Ca}^{2+}$), low pH ($\sim \text{pH} < 4.5$), high natural organic matter ($> 10 \text{ mg/L}$) and high intensity sunlight, ($> 2400 \text{ W cm}^2$ UVA daily) giving optimal conditions for CeO_2 toxicity. CeO_2 nanoparticles are a known additive for diesel fuel and diesel generation is the main source of power in these remote regions. The current study investigates the combined effects of NOM, CeO_2 NPs and sunlight on the responses cardinal tetras. CeO_2 NP were tested at 0.5, 1, 2 and 5 mg/L with or without sunlight. Expression of genes related to phase I and II biotransformation enzymes and reactive oxygen species generation and biochemical assays of ion transport and oxidative stress were measured to investigate if sunlight-mediated exacerbation of effects occurs.

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E-211

Single Cell ICP-MS Quantification of Metal Content in Individual organisms

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Applying Single Particle-ICP-MS (SP-ICP-MS) data acquisition concept with a proprietary introduction system designed to allow cells to enter the plasma of an ICP-MS individually is branded as Single Cell ICP-MS. This technique is opening new avenues to defining how cells react to metal and/or metallic components like nanoparticles at the cellular level eliminating the variability implied by cell viability and distribution. Advantages of Single Cell-ICP-MS include minimal to none sample preparation, rapid analysis, the ability to gain effective data from low concentrations of cells, and the ability to differentiate the ionic concentrations in the culture media from inside individual cells, removing the need for separating the cells from the culture media. As a result, Single Cell ICP-MS is promising great insights into cancer treatment, bioaccumulation and uptake of metals and/or nanoparticles by various by cells and small microorganism such as yeast, bacteria and algae ranging in size from 0.5 μm up to 100 μm .

As an example, consider the response of cancer cells to cisplatin, a common Pt-containing drug. It has been observed that although many cancer cells are initially responsive to cisplatin, they develop resistance over time by ejecting the drug. Therefore, the ability to monitor the Pt content of individual cells would help determine the effectiveness of treatment. Current methodology measures the platinum content of a population of cells, but does not provide any information about individual cells.

An initial study conducted using SC-ICP-MS shows that cellular uptake of cisplatin is heterogeneous, differs between cell lines but most important differs between the various cell cycles. Based on these initial results, SC-ICP-MS holds great promise for advancing the study of cancer treatments by monitoring the interactions of metal-containing anti-cancer drugs with cancer cells on an individual basis.

Effects of biosolids from a pilot wastewater treatment plant receiving manufactured nanomaterials on the model legume *Medicago truncatula*

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We examined the response of *Medicago truncatula* exposed to soil amended with biosolids produced from a pilot-scale wastewater treatment plant (WWTP) receiving a mixture of engineered nanomaterials (ENMs) or bulk/dissolved metals. We investigated two scenarios: The first scenario represented a realistic worst-case exposure, based on regulatory limits for metals in biosolids. Treatments included biosolids from a WWTP with either no metal introduced into the influent (control); bulk/ionic TiO₂, ZnO, and AgNO₃ added to influent (bulk/dissolved treatment); or Ag, ZnO, and TiO₂ ENMs added to influent (ENM treatment) and then added to soil, which was aged in the field for 6 months. The second scenario used currently predicted concentrations of ENMs in biosolids and bulk/dissolved controls. In the first scenario, only the ENM but not the bulk/dissolved treatment led to a significant decrease in microbial biomass and shifts in microbial community composition, decrease in plant biomass and root nodulation, as well as increased Zn uptake and Zn concentrations in shoots despite the fact that the speciation of the metals, as measured by X-ray absorption spectroscopy, was similar across treatments. In comparison with the bulk/dissolved treatment, exposure to the ENM treatment resulted in unique patterns in genes expression profiles and biological pathways associated with nitrogen metabolism, nodulation, metal homeostasis, and stress responses. These results suggested that these differences in toxicity were due to enhanced bioavailability of Zn in the ENM treatment resulting in phytotoxicity. The second exposure scenario resulted in no adverse effects on plant health compared to control or significant differences in metal uptake by plants among treatments. However, a change in soil microbial community composition and significant elevation in total microbial biomass were observed in ENM Low treatment relative to control. In summary, the results of these studies demonstrated that phytotoxicity can be caused by the exposure of the *M. truncatula* to biosolids containing ENMs at concentrations near regulatory limits for metals (the first scenario), while currently predicted concentrations of ENMs do not seem to affect adversely the plant health. However, in both scenarios, exposure to ENMs resulted in the shift of the microbial communities.

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Assessing the toxicity of polymer-coated magnetite nanoparticles, oil and their mixtures to a sediment dwelling marine invertebrate (Meiobenthic Copepod *Amphiascus tenuiremis*)

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Oil spills resulting from industrial wastes and maritime disasters have the potential to cause catastrophic damage to aquatic ecosystems. Crude oil and its fractions are a mixture of organic chemical species which can be highly toxic. When spills occur they need to be remediated as rapidly as possible to prevent ecosystem damage. Current oil remediation techniques are inefficient and may harm environmental habitats. However, new technologies including nanotechnology have been developed. Recently, a cheap and facile hydrothermal method was developed to synthesize polyvinylpyrrolidone coated iron oxide nanoparticles (PVP-coated iron oxide NPs) to remediate oil-contaminated waters successfully. In this study, PVP-coated iron oxide NPs, crude oil water accommodated fractions (WAF) and their mixtures were tested to determine the acute (4 day) toxicity to a sediment dwelling copepod *Amphiascus tenuiremis*. The NPs are very low in toxicity and no risk was likely, given likely deployment conditions, while the WAF is highly toxic. Mixing and removal of the NPs within 1 hour of exposure to copepods and WAF resulted in a > 90% reduction in toxicity compared to the WAF alone. Additions of NPs after the oil, while keeping both exposed to the NPs also resulted in reduced toxicity by about 10-40%. However, this approach has advantages which are currently being investigated.

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E-303

Effect of natural organic matter on the photo-induced toxicity of titanium dioxide (TiO₂) nanoparticles

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TiO₂ nanoparticles are the most widely used nanoparticles in commercial industry, and come in two main forms: rutile and anatase. Rutile TiO₂ is used in UV screening applications while anatase TiO₂ crystals have a surface defect that makes them photoreactive. There are numerous reports in the literature of photo-induced toxicity to aquatic organisms following co-exposure to anatase TiO₂ and UV. All natural freshwater contains varying amounts of natural organic matter (NOM), which can drive UV attenuation and quench ROS in aquatic ecosystems. The goal of this research was to examine how NOM alters the photo-induced toxicity of anatase TiO₂. *D. magna* neonates were co-exposed to NOM and photoexcited anatase TiO₂ for 48 hours. NOM concentrations as low as 4 mg/L reduced TiO₂ toxicity by nearly 100%. These concentrations of NOM attenuated UV by less than 10% in the exposure system. However, ROS production measured using a fluorescence assay was significantly reduced in an NOM concentration dependent manner. Taken together, these data suggest that NOM reduces anatase TiO₂ nanoparticle toxicity via an ROS quenching mechanism and not by attenuation of UV.

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AgNP Accumulation in Aquatic Organisms and Implications for Trophic Transfer

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Nanoparticles exhibit electronic spatial constraint, a large specific surface area, small size and high surface energy. These properties give them potentially novel environmental behaviors (Aufann et al. 2009; Croteau et al. 2011). Nanomaterials are currently used in electronic, biomedical and pharmaceutical drug design, cosmetics, nutrition supplements, energy applications and clothing manufacturing (Norwack and Bucheli 2007, Piccinno et.al. 2012) and NPs are known to be introduced into the environment through runoff and direct input. The U.S. National Nanotechnology Initiative (NNI), which includes several government agencies including the EPA, directed 5% of their yearly budget (over \$800 million) to research processes on the nanoscale in the environment as well as the environmental and social implications of nanotechnologies (Wiesner et al. 2006, Lin et al. 2012). Recent publications suggest that a complex mix of processes influences bioavailability and toxicity from metal-based NPs (Fabrega et al 2009; Croteau et al, 2014). For NP bio-uptake and bioavailability, the role of ions and particles has not been fully clarified, with reported studies often not conducting crucial measurements and basic measurements not currently validated to make appropriate distinctions at the nanoscale. A small number of studies reported complications such as concentration or size dependent dissolution (Zhang et al. 2011; Diedrich et al. 2012; Hadioui et al. 2013) and particle dissolution or re-precipitation under relevant biological exposure conditions (Tejamaya et al. 2012). It is assumed, with some collaborating data (e.g. Franklin et al. 2007) that toxicity of soluble NPs such as ZnO, is controlled by dissolution. Conversely, insoluble NPs such as ceria have low solubility, and the assumption is that the ion plays little role, although this may not always be the case (Roehder et al. 2014). Other NPs such as silver are partially soluble and reports suggest either mainly ion or mainly particle behavior (Navarro et al. 2008; Fabrega et al. 2009; Xiu et al. 2012). The impacts of NP dissolution on bioavailability and bio-uptake remain highly uncertain and the proposed novel core-shell NPs and biodynamic model allows a full interpretation of the role of dissolution and uptake. This study uses *Prorocentrum minimum*, an estuarine dinoflagellate, and *Crassostrea virginica*, the Eastern Oyster, to determine the mechanism of bioavailability of silver NPs and the consequent role this plays on trophic transfer and toxicity. The following questions are addressed by this research: 1) Is NP bio-uptake and bioavailability mediated by the particle or by free ions? 2) If both forms contribute to bioaccumulation, can their relative

contributions be differentiated? This study will greatly improve the understanding of how bioaccumulation and toxicity manifest under environmentally realistic conditions.

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In vitro interactions of silver nanoparticles on Human Peripheral Blood Mononuclear Cells (PBMC)

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Silver nanoparticles (AgNPs) are the most commonly used nanoparticles in consumer products including in medical applications such as wound dressing, bandages and bone prostheses due to their antimicrobial properties. As soon as nanoparticles enter the body, they will be translocated to and by the circulatory system and come in direct contact with cells in the blood, and ultimately be distributed and accumulated in organs. The impact of silver on the immune system is not fully understood. There are few of studies which analyze the potential cytotoxicity and cellular response of human blood cells exposed to AgNPs. It is also unclear whether the measured toxicity is due to metallic silver or the ionic silver form. The overall aim of this project is to delineate the effect of AgNPs from Ag ions on human peripheral blood mononuclear cells (PBMC). We exposed PBMCs to a range of low and physiologically relevant concentrations (1-1000 $\mu\text{g/l}$) of AgNPs coated with polyvinylpyrrolidone (PVP), or controls (silver nitrate (AgNO_3) and PVP). Cells were either stimulated with LPS (lipopolysaccharide) or unstimulated, cultured with AgNPs or controls for 24 hours. Experiments included tissue culture media supplemented with fetal bovine serum (FBS) or in serum-free conditions. The supernatant and cell pellets were collected for analysis. The cell culture supernatant was examined for cytokine release ($\text{TNF-}\alpha$ and $\text{IL-1}\beta$, pro-inflammatory cytokines released from activated macrophages) and Ag concentration by ICP-MS. SP-ICP-MS was used on the pellet to measure single nanoparticles in the cells. Cytotoxicity was determined by MTT assay. In 100 $\mu\text{g/l}$ AgNO_3 we found almost 50% decrease in cell viability, and decrease in $\text{IL-1}\beta$ secretion in LPS-stimulated cells cultured in serum-containing media, compares to control. At the same concentration in serum-free media we found a decrease in cell viability but increase in cytokine production in LPS-stimulated cells compares to control (control is 0 $\mu\text{g/l}$ AgNO_3 , LPS-stimulated cells). We did not realize any significant decrease in cell viability when cells were exposed to PVP coated AgNPs. Results will be presented for accumulation and toxicity of AgNPs in PBMCs relative to control treatments.

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Poly (acrylic acid) polymer coating mitigates hydroxyl radical-mediated effects of titanium dioxide nanoparticles in developing zebrafish (*Danio rerio*)

Lindsey Felix, University of Alberta
Erik J. Folkerts, Yuhe He, Greg G. Goss; University of Alberta

Widespread production of titanium dioxide nanoparticles (TiO₂ NPs) for use in various consumer products has increased the potential for their release into the environment. Most studies examine TiO₂ NP toxicity under laboratory lighting that emits little to no ultraviolet (UV) radiation, yet these nanoscale particles are band gap semiconductors capable of generating reactive oxygen species. The purpose of this study was to examine the *in vivo* effects of polymer coating on TiO₂ NP phototoxicity. Zebrafish (*Danio rerio*) embryos were exposed to 0.1, 1 or 10 mg/L of uncoated and polymer coated TiO₂ NPs, as well as the polymer coating alone, in the presence and absence of UV light. Survival, hatching success, malformation, thiobarbituric acid reactive substances, catalase activity, total glutathione, superoxide dismutase activity, and alteration in gene expression were measured. While uncoated TiO₂ NPs produced hydroxyl radicals ($\cdot\text{OH}$), delayed hatch, and upregulated glutathione peroxidase 1a gene expression in the presence of UV light, these effects were not observed with polymer coated TiO₂ NP and UV light coexposures. We suggest that the polymer coating mitigates $\cdot\text{OH}$ -mediated effects of TiO₂ NPs in developing zebrafish and that toxicity depends on UV illumination.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
E-307

Chlamydomonas reinhardtii display aversive swimming response to silver nanoparticles

Nicholas Lin, McGill University
Michael R. Mitzel (McGill), Joann Whalen (McGill), Nathalie Tufenkji (McGill)

In this study, the freshwater microalgae *Chlamydomonas reinhardtii* was exposed to linear gradients of silver nanoparticles (nAg) using a microfluidic device designed for the study of swimming chemotaxis. Swimming was monitored visually using an enhanced dark-field hyperspectral microscope at 1000 μm increments over the 14,000 μm exposure channel. At a flow rate low enough to allow for free, but directed, swimming (0.55 $\mu\text{L}/\text{min}$), video analysis of swimming indicated that *C. reinhardtii* displayed a significantly different swimming trajectory away from nAg concentrations at and above 10^8 nAg particles/mL. Conversely, the algae displayed no directed avoidance to 1 μM silver nitrate (Ag^+); though the variance in algae position nearly tripled at 10 μM . 10^7 nAg particles/mL algae displayed no significant avoidance behaviour, while at 1×10^{10} nAg particles/mL *C. reinhardtii* showed drastically reduced motility. Additional experiments performed using sulfate latex nanoparticles indicated that a significant avoidance response to these relatively inert particles was also observed at and above 10^{10} particles/mL. The evidence presented here suggests that *C. reinhardtii* are able to detect and avoid silver nanoparticles rapidly (under 30 sec) and that this avoidance swimming response is related to the frequency of collisions between cells and nAg. At the conditions investigated, *C. reinhardtii* appear to display avoidance to nAg when the likelihood of a particle collision is approximately 1 in 1,000, while this avoidance occurs at approximately 1 in 100,000 for latex nanoparticles. These findings illustrate that the heterogeneity inherent to particle suspensions may allow organisms to detect and avoid nanoparticles.

Proteomic analysis to study the interaction of engineered nanomaterials with plants and implications on the food chain

Sanghamitra Majumdar, Connecticut Agricultural Experiment Station

The rapidly expanding applications of nanocerium ($nCeO_2$) in biomedicine, agriculture, automotives, and electronics, demand rapid toxicological assessment with different ecological receptors. There is currently inadequate information on particle impact on plant biochemistry, food quality and the cellular mechanisms associated with nanotoxicity. Bottom up-proteomics is well suited for detecting subtle responses at the cellular and molecular level that are often too sensitive to be detected by existing biochemical and physiological parameters. The differential expression analysis of identified proteins as compared to unexposed controls gives a definitive measure of nanotoxicity and enable identification of biomarkers of exposure. In our study, kidney bean plants (*Phaseolus vulgaris*) were grown in soil varying in organic matter (OM) content that had been amended with 0-500 mg/kg $nCeO_2$. After a full life cycle exposure, plant metabolic activities, antioxidant enzyme activity, and plant yield were assessed. Cerium content in the root, shoot and pod tissues were measured. In the harvested seeds, shotgun proteomic analyses were performed using liquid chromatography tandem mass spectrometry (LC-MS/MS). Soil OM content modulated the response of $nCeO_2$ on stomatal conductance, photosynthesis rate and respiration, and plant yield. Translocation of Ce to the leaves was significantly higher (71%) in plants grown in high OM than in LOMS at 500 mg/kg $nCeO_2$. Cerium was also translocated to the filial tissues; a dose -dependent accumulation was observed in the seeds harvested from plants grown in high OM soil. As revealed through proteomic analysis, defensin and purple acid phosphatase synthesis were up-regulated at 125 and 250 mg/kg $nCeO_2$, primarily associated with stress response and nutrient acquisition. However, the number of down-regulated proteins increased in dose-dependent manner. Down-regulated proteins were associated with seed metabolic activities, nutrient storage, micronutrient binding and accumulation as well as energy transfer. The trophic transfer of Ce (nanoparticle and bulk) from kidney bean tissues to the Mexican bean beetles and then to spined soldier bugs was also investigated. Ce accumulation in individual plant tissues was independent of particle size and or exposure duration. The beetle larvae feeding on $nCeO_2$ exposed leaves for 7 days accumulated low levels of Ce due to excretion of ~98% of the ingested Ce. However, in later growth stages, the adult beetles accumulated 76% more Ce in the $nCeO_2$ exposure than from the bulk particles, suggesting particle size-dependent trophic transfer. Particle-size and exposure duration dependent biomagnification was observed from plants to adult beetles and further to spined

soldier bugs. Related studies on proteomics and trophic transfer are being evaluated in different systems.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
E-309

Differential Cytotoxicity of NiO and NiOH Nanoparticles in HepG2 and A549 Cell Lines

Melissa Cambre, Missouri University of Science and Technology
Yue-Wern Huang

Nanomaterials have become increasingly popular in the production of a wide range of products including cosmetics, pharmaceuticals, cancer research, printer toners, food, electronic manufacturing, and many other products. Different nanoparticles possess different levels of toxicity depending on their chemical and physical properties. In this study, we hypothesize that 1) NiO and NiOH exhibits differential cytotoxicity and 2) physiochemical properties of nanoparticles dictate the difference. The specific surface areas of NiO and NiOH are 73.45 m²/g and 103.17 m²/g, respectively. Surface charge of NiOH is neutral in cell media while NiO is slightly negatively charged. NiOH has a hexagonal shape and NiO has a cubic shape. Cell viability studies showed that NiOH is 20%-40% more toxic in HepG2 cells (a liver cell line) and A549 cells (a lung cell line) in 24 and 48-hour exposure times. We are in process of determining size, morphology, relative number of surface binding site of particles, dissolution rate of Ni from NiOH and NiO. Meanwhile, we are investigating various effects induced by nanoparticles which include oxidative stress, lipid peroxidation, inhibition of cell proliferation, and alteration of cell cycle analysis.

The Interactive Effects of UV Radiation and Titanium Dioxide Nanoparticles on Marine Snow-Associated Microbes

Vena Haynes, University of Connecticut

Titanium dioxide nanoparticles (TiO₂ NP) are used in a variety of consumer goods including paints, sunscreens, skin-care products and anti-microbial agents. As a result of their prevalent use, especially related to beach and boating activities, TiO₂ NP are likely entering the marine environment via direct and indirect inputs. Nanoscale TiO₂ NP are photocatalysts, able to produce reactive oxygen species (ROS) that can damage living cells and cause deleterious effects in some aquatic organisms. As with other suspended particulate matter, NP can be incorporated into natural agglomerations (e.g., marine snow) through association with other particles. This study investigated the effects of two types of commercially available TiO₂ NP (UV-Titan and Degussa P25) on marine snow-associated microorganisms. Natural seawater was spiked with either UV-Titan or P25 NP at a concentration of 0.5 mg l⁻¹ and marine snow was generated by means of a roller table. During the 3-day rolling period, seawater and associated microbes were exposed to three different light regimes (15-hr light, 9-hr light and 0-hr light as a control) at two different irradiance levels (corresponding to typical values found in coastal waters). Light was supplied by solar lamps that mimic natural light in the visible and UVA/B regions. An oceanographic optical model, Hydrolight, was used to determine the appropriate environmental light levels for experiments. Marine snow was collected and bacterial abundance (CFU ml⁻¹) and bacterial functional diversity (EcoPlates) were analyzed. A shift in bacterial functional diversity occurred for light treatments compared to controls (NP treatment in the dark, light treatment without NP), suggesting that the two types of NP can have toxic effects on marine snow-associated organisms under environmentally relevant light regimes. By exposing marine snow organisms to NP under light and dark treatments, we were able to separate photocatalytic effect from nanoscale-size effects. This study provides valuable information on the performance of widely used NP under realistic environmental conditions and could aid in the development of safer nanomaterials.

Intergenerational studies on the effects of cerium oxide nanoparticles in wheat

Cyren Rico, US EPA
Christian P. Andersen

The intergenerational impacts of engineered nanomaterials in plants are not yet well understood. A soil microcosm study was performed to assess the physiology, phenology, yield and nutrient uptake in wheat (*Triticum aestivum*) exposed to nanoceria (nCeO₂). Seeds from parental plants that were exposed to 0, 125, and 500 ppm nCeO₂ in soil at first generation (S1) were cultivated at factorial combinations of either 125 or 500 ppm nCeO₂ treatment to produce second generation treated plants (S2). The factorial combinations for first/second generation treatments with 125 ppm nCeO₂ were S1-Ce-0/Ce-0, S1-Ce-0/Ce-125, S1-Ce-125/Ce-0 and S1-Ce-125/Ce-125, and for 500 ppm nCeO₂ were S1-Ce-0/Ce-0, S1-Ce-0/Ce-500, S1-Ce-500/Ce-0 and S1-Ce-500/Ce-500. Agronomic data was collected and plant tissues were harvested for elemental and isotopic analyses. Results showed that S1 exposed plants had accelerated growth and earlier grain formation; however, there was no significant difference in grain yield during harvest. Isotopic analysis revealed that there were differences among treatments in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. Relative to control, both 125 and 500 ppm nCeO₂ treatments produced grains that had lower $\delta^{15}\text{N}$ in S1 stressed plants but higher $\delta^{13}\text{C}$ in S2 treated plants. Surprisingly, elemental analysis showed that nCeO₂ treatment reduced uptake of Ce in plants. S1 stressed plants accumulated less Ce compared to S1 unstressed plants. In roots, S1-Ce-125 and S1-Ce-500 had 67 and 39% lower cerium concentration, respectively, compared with S1 unstressed plants. Similarly, nCeO₂ treatment at first generation resulted in lower uptake of Fe and Mn in roots. In S1-Ce-125 and S1-Ce-500, the Fe concentration decreased by 51 and 46%, respectively, while Mn decreased by 27 and 21%, respectively, compared to S1 unstressed plants. In summary, the study revealed that previous generation exposure of wheat to nanoceria had carry-over effects on the physiological and agronomic responses of the succeeding generation.

Wednesday, August 16/Thursday, August 17, 2016
Poster Session III
E-312

Colloid Transport In A Microfluidic Soil Analog: Population Dynamics And Single Particle Trajectories

Yang Guo, Colorado School of Mines

Low solubility contaminants such as heavy metals and radionuclides can adsorb onto mobile colloids and travel with underground water in soils over kilometers. However, the detailed flow pathway and rate-limiting transport mechanism of colloids in soils are largely unknown. To study these phenomena we developed a microfluidic soil analog to measure both population dynamics and single particle trajectories of model colloids. The soil analog consists of an $O(1 \text{ mm}^2)$ chamber filled with packed $15 \mu\text{m}$ polystyrene beads. Comparisons between measured and estimated hydraulic permeability from Lattice Boltzmann Method (LBM) simulations suggest a pseudo-two dimensional packing with $\sim 50\%$ of beads displaced from the bottom of the channel. A T-junction at the exit of soil analog allowed for encapsulation and enumeration of several thousand colloids per experiment to give population dynamics. Single particle trajectories of 0.5 , 1 , and $3 \mu\text{m}$ colloids were captured by fluorescence microscopy within the soil analog at Peclet numbers of 1600 - 9600 . Tortuosity calculated from these trajectories and comparison with LBM simulations using point particles revealed that pore-scale transport of colloids was influenced by the size exclusion effect. The innovative features of this device provide a means to link microscale transport properties like particle trajectories, which are difficult to measure in natural soils, to macroscale transport properties like dispersion, which can be measured in column and field-scale experiments. This device will enable future studies to connect micro- and macroscale colloid transport and to measure the effect of chemical heterogeneities that mimics those found in natural soils.

Invited Speakers List



Tuesday, August 16, 2016
Invited Speaker
1:20 PM

Effect of nanomaterial and media physicochemical properties on nanomaterial aggregation kinetics

Mohammed Baalousha*

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Aggregation is a key process affecting nanomaterials (NMs) environmental fate, uptake and effects. Understanding nanomaterial (NM) stability is required for an adequate interpretation of ecotoxicological test outcomes, fate and behavior studies, to generate parameters (such as critical coagulation concentration, CCC; and attachment efficiency, α) for environmental fate models, and for comparison among different studies. Numerous studies measured CCC and α for different types of NMs with a major focus on investigating the effect of ionic strength, ion valency and natural organic matter, with fewer studies investigating the effect of NM and other medium properties. Consequently, wide discrepancies can be found in the literature among the reported CCC and α values, even for NMs of the same composition and properties.

As such, this presentation will discuss the effect of NM and medium physicochemical properties on NM aggregation kinetic parameters (e.g. CCC and α), and will rationalize the differences observed among different studies, where possible. NM and medium properties such as NM composition, crystal structure, morphology, size and dispersity, surface coating and coverage, surface heterogeneity and roughness, buffer concentration, dissolved oxygen, light, and temperature are all important factors determining NM stability in addition to the typically studied medium properties such as ionic strength, valency and natural organic matter type and concentration.

Monday, August 15, 2016
Invited Speaker
9:00 AM

The challenge of modeling coupled techno-ecological impacts across the engineered nanomaterial life cycle

Callie Babbitt

Golisano Institute for Sustainability, Rochester Institute of Technology

Engineered nanomaterials enable new technologies that have the potential to transform society. But these benefits may come at a high cost if their production, use, and disposal systems are designed and managed without proactively considering potential environmental and human health risks. The method of life cycle assessment (LCA) offers a holistic, “cradle-to-grave” approach to quantifying energy and material inputs, emission and product outputs, and attendant ecological and health impacts across the entire ENM production chain. However, the current state of practice in nano-LCA still faces a number of methodological challenges, which limit its usefulness at informing sustainable management practices. For example, nano-LCA often focuses on energy and resource use associated with the production of a specific nanomaterial, but rarely compares these environmental costs to the potential benefits of the material’s integration into an end-use application, like the increased energy efficiency of nano-enabled solar cells. Life cycle nanomaterial impact analysis still requires greater development of ecotoxicity and ecosystem-level impact assessment models, but these advances must also allow for comparisons to displaced pollution associated with nano-enabled product or process improvements, which may include more well-characterized releases, like greenhouse gas emissions or criteria pollutants. Using examples from carbon nanomaterial integration into renewable energy systems, this presentation will overview and illustrate challenges and opportunities for advancing nano-LCA practice for more effective sustainability assessment of emerging nanotechnologies.

Tuesday, August 16, 2016
Invited Speaker
9:00 AM

Current challenges in spICP-MS analysis of engineered nanoparticles in environmental samples

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Single particle ICP-MS has grown fast in recent years as a technique to analyse size and number concentration of nanoparticles in particularly difficult samples and at environmentally relevant concentrations. The technique has grown in a fast rate from proof of principle, exploring to now being more and more applied and commercial ICP-MS manufacturers providing spICP-MS features. However, the development stage of spICP-MS has not finished and the technique is still faced with several challenges, partially posed by the on-going quest to ever expand the capabilities of spICP-MS. Some of these concern hardware development, but algorithms and correct interpretation of spICPMS data has been developing.

The current presentation will give an overview of the most recent developments in analysis of environmental samples in spICP-MS and which challenges remain. The limited dynamic range and accuracy of spICP-MS has seen such an evolution, where more recently, the short dwell times of FAST spICP-MS have provided improvements. It is similarly discussed how the size dynamic range has been improved by several means. Other analytical issue, such as the occurrence of interferences and drift and how to resolve these are discussed. Finally, extensions of spICP-MS, such as hyphenation with other techniques, that seek to expand the possibilities of the technique.

Wednesday, August 17, 2016
Invited Speaker
9:00 AM

Novel uses of enriched stable isotopes to assess the bioavailability of metals, including metal-based nanoparticles

Marie-Noele Croteau, USGS Menlo Park

The potential for bioaccumulation and toxicity of a number of nanoparticles (NPs) has been established. However, risk to the environment is poorly characterized. The sustainability of this beneficial industry requires greater understanding of risks and minimization or mitigation of these risks. For metal-based NPs like silver (Ag) NPs, the role of ions and particles for bioaccumulation and toxicity has not been fully elucidated. One of the most important unknowns is whether NP impacts depend upon their dissolution. If they must dissolve to be toxic, then the issue is similar to other contaminants like metals. However, if the nanoparticle itself is taken up by organisms and humans, then novel impacts are possible. To date differentiation of these two possibilities has been addressed only indirectly. Studies have used models or correlations to infer that the direct particle bioavailability can be important. A second problem is that, despite the poor understanding of impacts, a new generation of multiple metal NPs is being produced. New tracer approaches can help address both the particle uptake and the multiple metal NP questions. Enriched stable isotopes have the potential to overcome many of the shortcomings of radioactive tracers, and their application is growing rapidly as a result of new developments in mass spectrometric instrumentation, especially inductively coupled plasma mass spectrometry. This presentation will describe novel uses of enriched stable isotopes in ecotoxicology, especially in studies aiming to characterize the bioavailability of metals, and the processes that control bioavailability. A novel and nontraditional use of stable isotope tracers to study metal bioavailability from natural particles will also be presented.

Thursday, August 18, 2016
Invited Speaker
1:20 PM

**Biological and Environmental Media Control Oxide Nanoparticle
Surface Composition: The Roles of Biological Components
(Proteins and Amino Acids), Inorganic Oxyanions and Humic
Acid**

Vicki Grassian
University of California San Diego

Developing nanotechnology in a sustainable way requires fundamental understanding of how nanomaterial properties affect their reactivity, environmental fate, and toxicity in a range of environmental and biological media/systems. It is well known that nanoparticle surfaces have high free energy and therefore thermodynamic driving forces will work toward minimizing the surface energy. In order to achieve a lower energy state, nanoparticles undergo different physical and chemical transformations including surface reconstruction, aggregation, dissolution and ligand adsorption. In environmental or biological systems, the surrounding milieu will drive these interactions. Therefore it is important to consider nanoparticles as dynamic entities that undergo rapid transformations that depend on solution pH, ionic strength and composition. A focus of this talk will be to highlight a few examples of in situ characterization of oxide nanoparticle surfaces in different environmental and biological media so as to show the importance of the milieu on surface composition. The surface composition is shown to be vastly different in different media with adsorption of biological components (proteins, peptides and amino acids), inorganic oxyanions and humic acid occurring. The extent of surface adsorption depends on the solution phase composition and the affinity of different components to adsorb to the nanoparticle surface. For protein adsorption, it will be shown that the secondary structure changes with biologically and environmentally relevant pH and for different types of oxide nanoparticles. As will be discussed, protein-nanoparticle interactions are strongly dependent on pH and specific nanoparticle-surface interactions.

Monday, August 15, 2016
Invited Speaker
1:20 PM

Bacteria Interactions with Nanoscale Battery Materials

Christy Haynes, University of Minnesota
Ian Gunsolus, Mimi N. Hang, Natalie Hudson-Smith, Joseph T. Buchman, Robert
J. Hamers, Christy Haynes

Nickel manganese cobalt oxide (NMC) is a class of lithium intercalation compounds of emerging importance in nanoparticle form as cathode materials for lithium-ion batteries. To evaluate the potential environmental impact of release of this material in the environment, we synthesized NMC nanosheets and investigated their interaction with two bacterial strains: *Shewanella oneidensis* and *Bacillus subtilis*. Exposure to NMC significantly impaired bacterial population growth and respiration, dependent on the incongruent material dissolution and measurable release of all four metal constituents (Li, Mn, Co, and Ni) into solution. The largest impacts arose from Ni(II) and Co(II) species.

Thursday, August 18, 2016
Invited Speaker
9:00 AM

Potential Applications of Nanotechnology in Agriculture and Crop Protection

Jeffrey S. Murray, Regulatory Strategy Manager
BASF - Agricultural Solutions, Research Triangle Park, NC

Global agriculture faces significant challenges in the coming decades to ensure sufficient food for a population that is projected to peak at 9.1 billion by the year 2050. Arable land is either static or decreasing in developed countries due to urbanization, climate change mitigation, and habitat preservation. The 70% increase in global food supply that will be needed to feed the world population can only be achieved by increasing crop yields.

For the past 75 years, crop protection products (pesticides), fertilizers, and genetics have been instrumental in increasing crop yields. Innovation is needed to increase yields beyond what they are today while also protecting the environment.

Nanotechnology represents a new and important tool for agriculture. For example, the unique chemical properties of nanomaterials could help to reduce the effective number and/or rate of application of nutrients or pesticides which ultimately reduces exposure risks to pollinators and other non-target organisms. Nanotechnology may also allow for targeted and controlled release of pesticides, ensuring that the pesticide, needed for protecting crop yields, is present at the right location and at the right time. Nanotechnology could be used to facilitate plant uptake of fertilizers which could reduce the potential for fertilizer runoff to surface water and ground water.

Innovations in crop protection and fertilizer products will be critical for ensuring global food security through 2050. We expect nanotechnology to play an important part in agricultural advancements that contribute to this important goal.

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