

Nanoparticle Air Monitoring – Technology Needs and Gaps

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March 2, 2009



1. How applicable are the existing size measurement instruments? Are these sufficient?
2. What characteristics (physical and chemical) should we focus on to identify and quantify nanoparticles?
3. Should the focus be anthropogenic or naturally occurring particles?
4. What considerations should be made about fate and transport?
5. Should we try to classify these particles into some types or groups?
6. Do we need real-time measurement techniques?

Nanoparticle Air Monitoring Workshop, RTP, NC, 03/02-03/2009

What characteristics (physical and chemical) should we focus on to identify and quantify nanoparticles?

- **Examples (3) of airborne nanoparticles**
 - What's been observed
- **Biological connection**
 - What's known
- **Gaps and needs**

Combustion Engines Emissions



- Carbon-based particles
- Complex chemical composition
- Capacity to phase partition

- Structural aggregate
- Embedded nanostructure
- Large ultrafine fraction

- Sampling challenges
- Biologically toxic
- Implied nanotoxicity

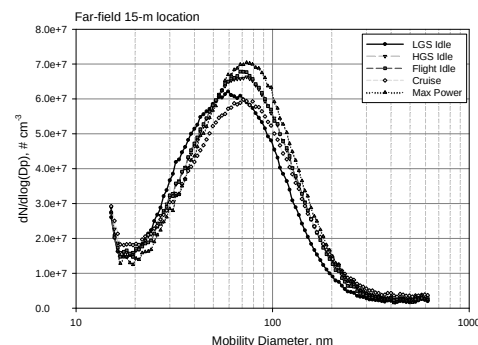
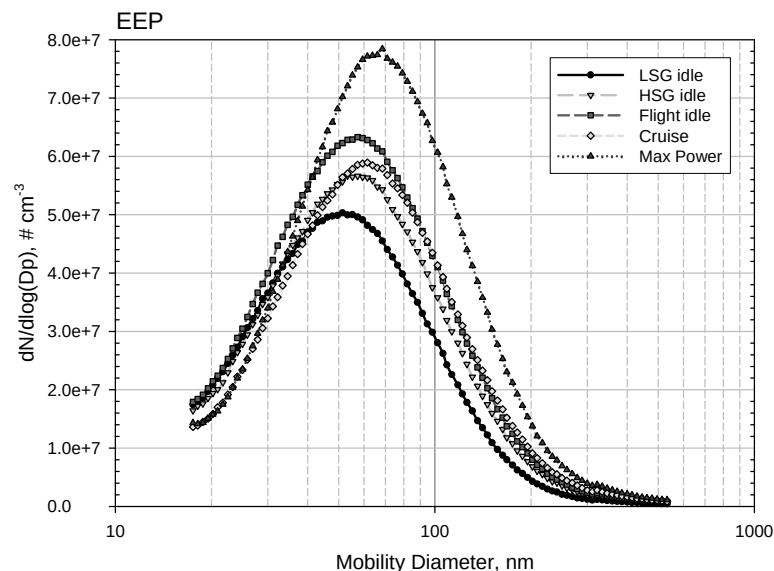
Turbine Engine Emissions of Ultrafine Particles



- Dilution probe sampling at EEP
- Dilution corrected for samples taken at 15-m downstream
- Peak in ultrafine range
- Peak grew as power increased
- Things to pay attention
 - Sampling loss
 - Instrument calibration

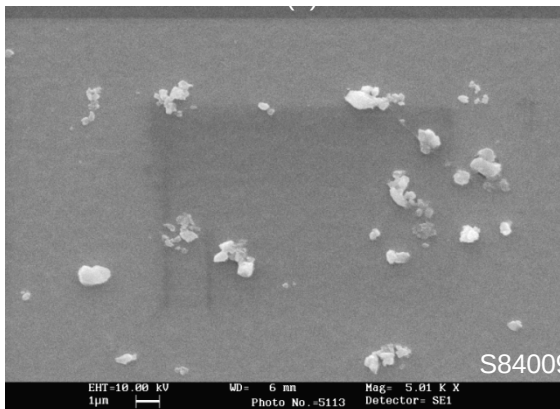
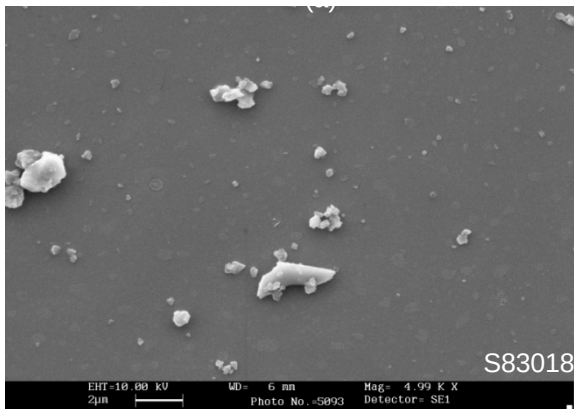
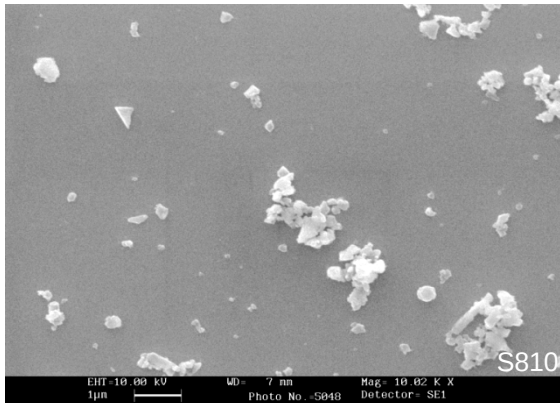
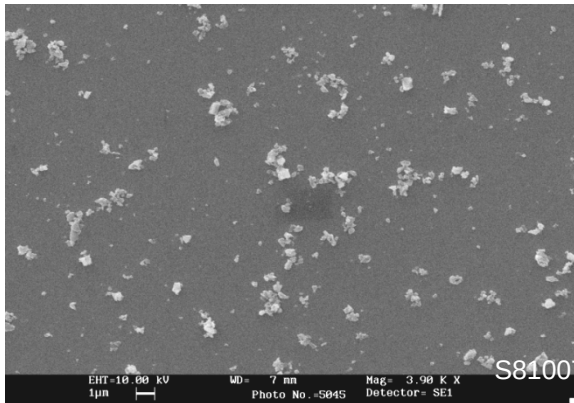
Attributes as a function of engine power

- Size, size distribution
- Number and mass concentrations
- Chemical species
- Soot microstructure



Be and BeO System

Testing real-time Be monitor at a nuclear complex



- Simpler chemical composition
- Highly toxic
- Polydisperse
- Nonspherical
- Significant ultrafine fraction

Source: Cheng et al., JASTMI, 2006, 3(1), JAI13172

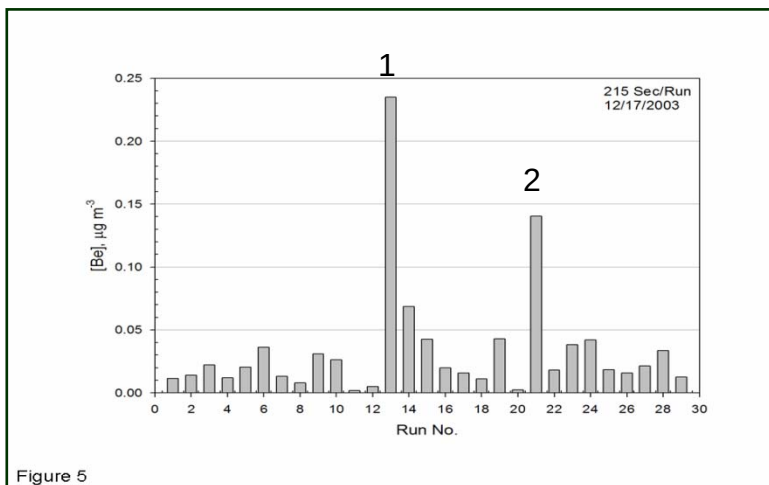


Figure 5

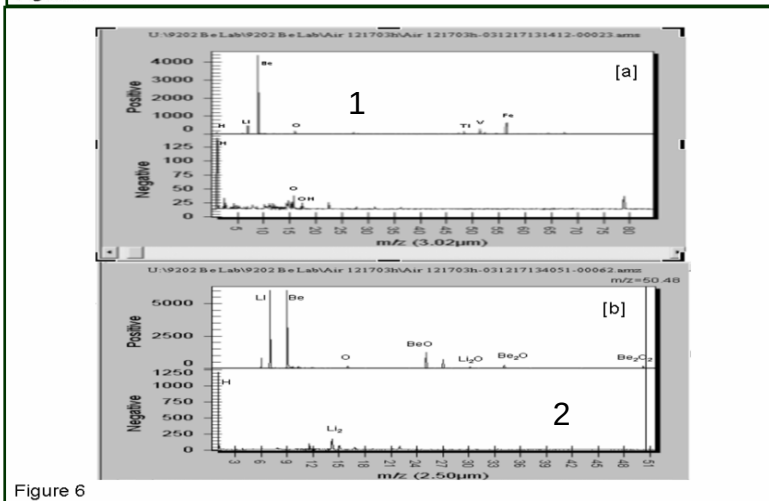
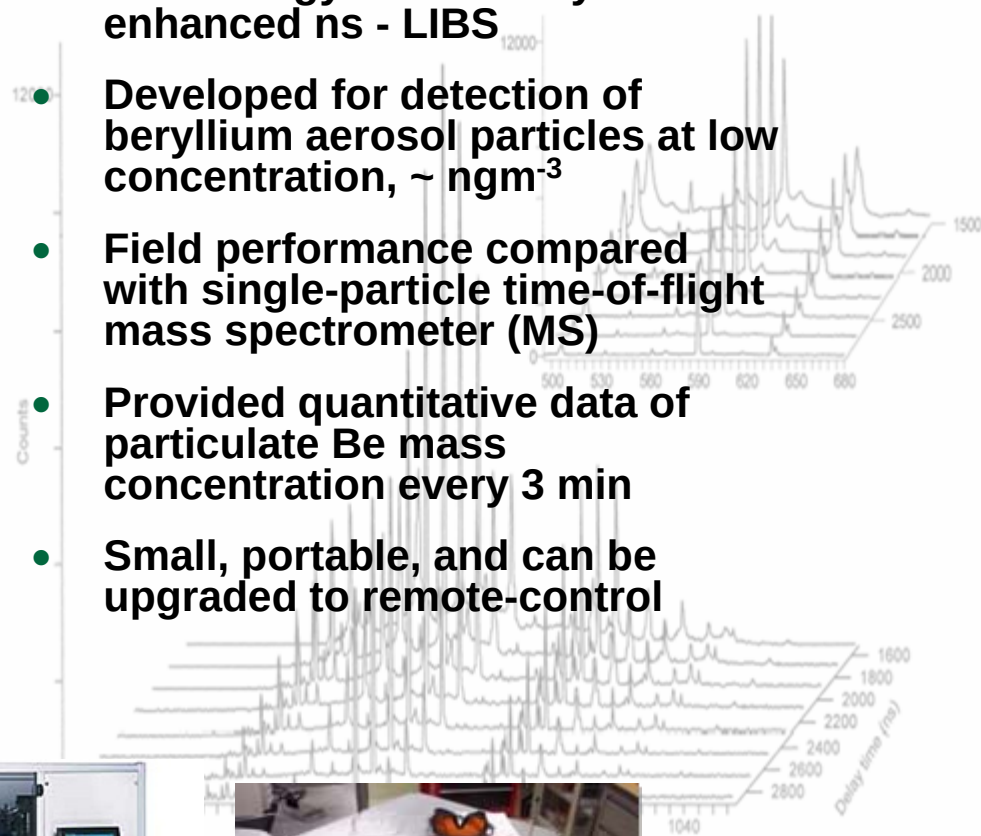


Figure 6

- Real-time monitor for workplace alarm function of Be particle incursion
- Technology: Electrically enhanced ns - LIBS
- Developed for detection of beryllium aerosol particles at low concentration, $\sim \text{ngm}^{-3}$
- Field performance compared with single-particle time-of-flight mass spectrometer (MS)
- Provided quantitative data of particulate Be mass concentration every 3 min
- Small, portable, and can be upgraded to remote-control

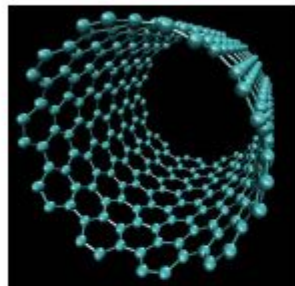


•Source: Cheng, Smithwick, and Hinton, JASTM, 3(1): JA113172, Jan. 2006

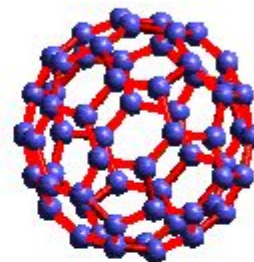


Nanomaterials

Single and multi walled nanotubes



Fullerenes



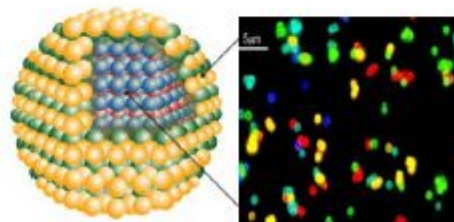
Metal oxides



Dendrimers



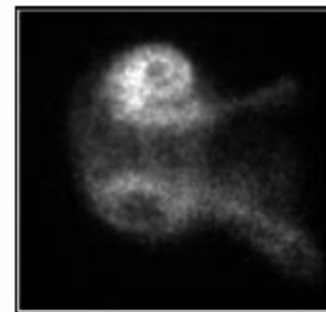
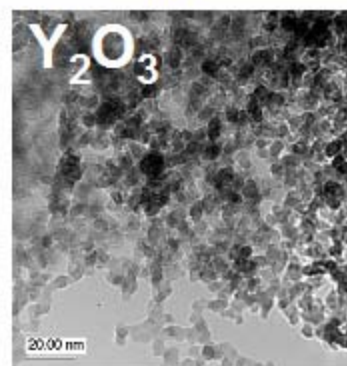
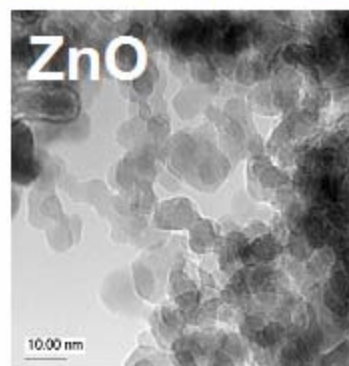
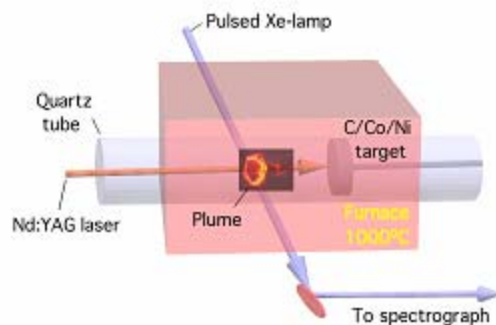
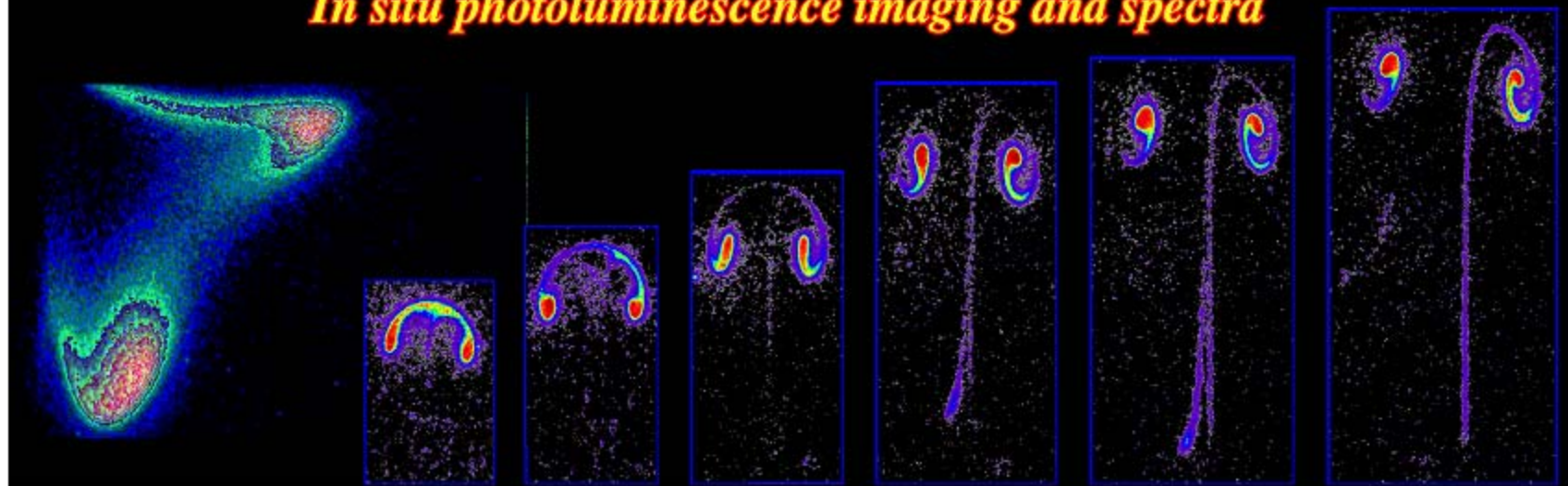
Quantum dots



Slide courtesy of Nigel Walker NIEHS/NTP

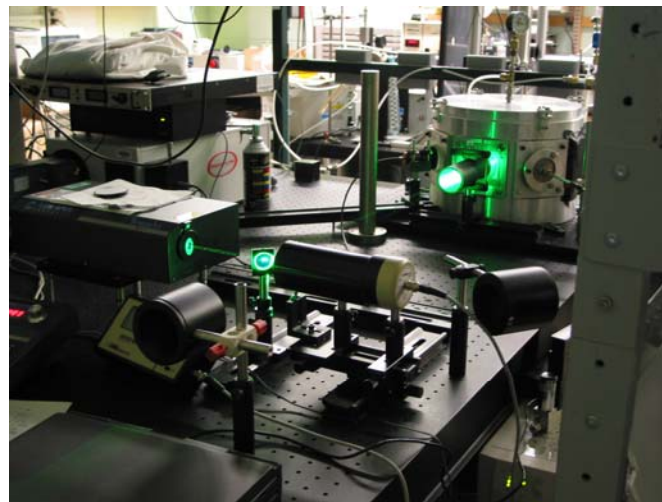
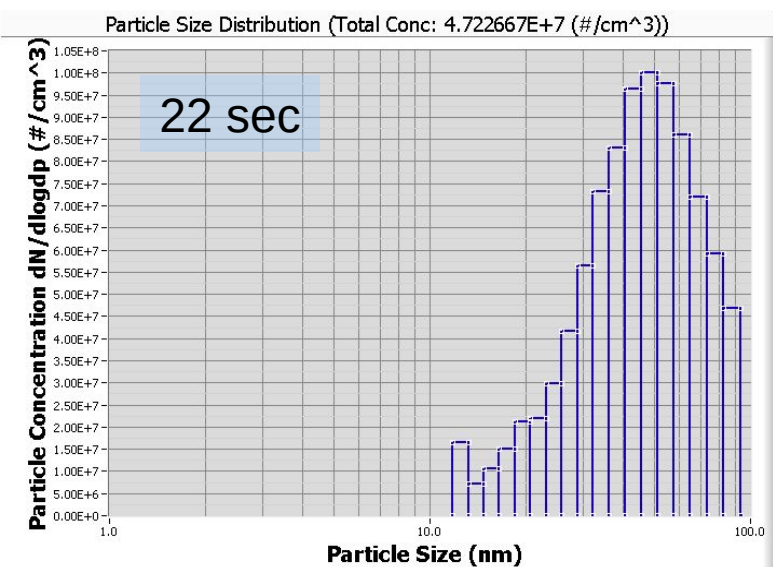
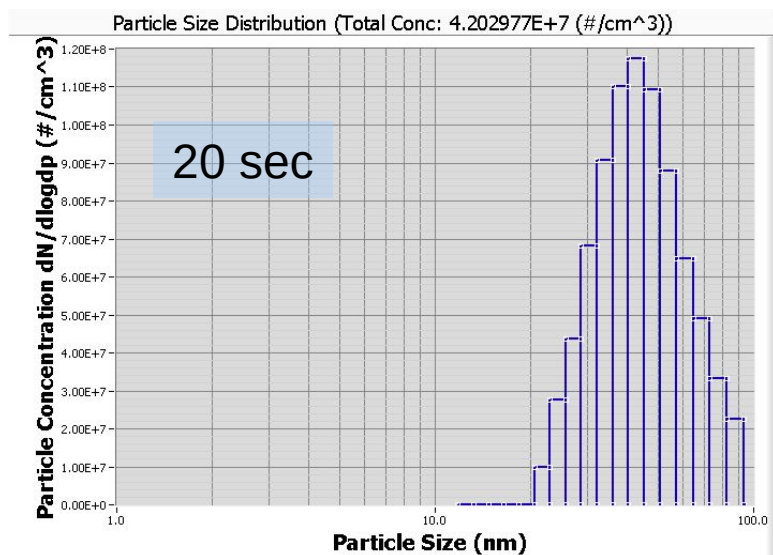
Compared with the last two categories, their sizes are all about on the same order. Beyond that, nanomaterials have nothing in common to the other two.

Dynamics of Nanoparticle Synthesis by Laser Ablation: *In situ photoluminescence imaging and spectra*



"Photoluminescence from Gas-Suspended SiO_x Nanoparticles Synthesized by Laser Ablation", D. B. Geohegan, A. A. Puretzky, G. Duscher, and S. J. Pennycook, Appl. Phys. Lett. 73, 438 (1998).

"Gas-Phase Nanoparticle Formation and Transport During Pulsed Laser Deposition of Y₁Ba₂Cu₃O_{7-d}", D. B. Geohegan, A. A. Puretzky, and D. J. Rader. Appl. Phys. Lett. 74 3788-3790 (1999).



- Continuous monitoring of size distribution
- DMA classification 1 curve per 2 sec
- Yielded data on rapid transition in laser-ablation particle synthesis

Lee and Cheng (2006), JAWMA, 56:1591; Lee and Cheng (2004a) J Aerosol Sci., 35:1527
 Lee and Cheng (2004b) J. Aerosol Sci., 35:1513; Qi, Chen, and Cheng (2007) JAAQR, 7(1): 1

Particle Deposition Pattern

Annals Biomed. Engr., (2009) 37: 271

CFD Simulation of Aerosol Deposition in an Anatomically Based Human Large-Medium Airway Model

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Department of Biomedical Engineering, Boston University, 44 Cummington Street, Boston, MA 02215, USA

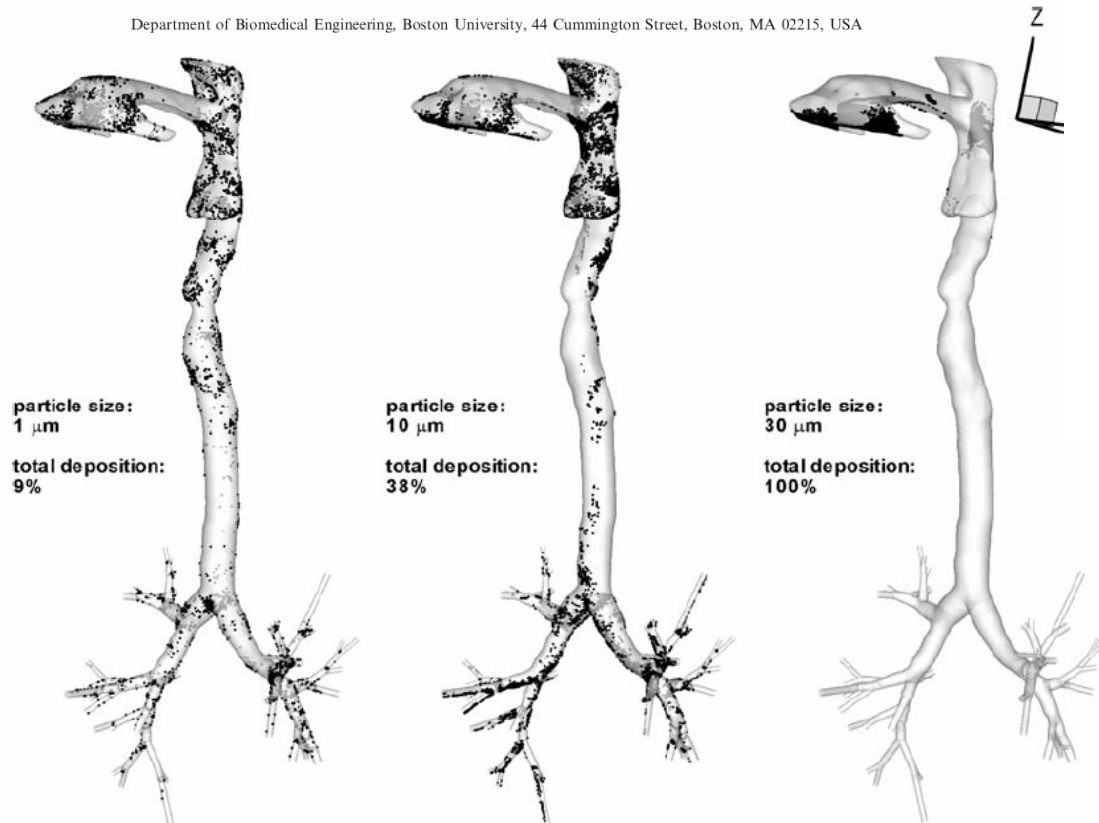
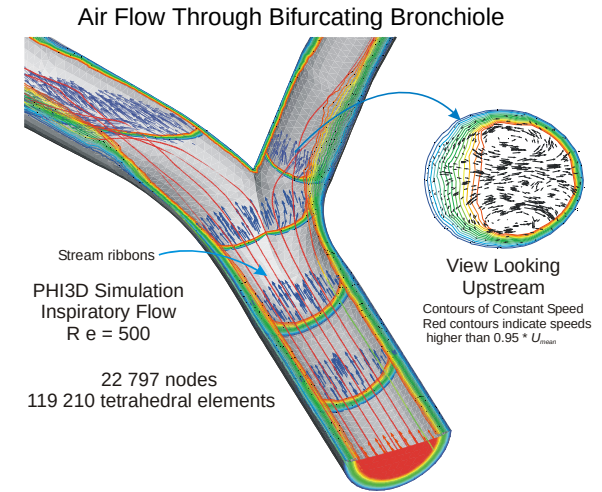


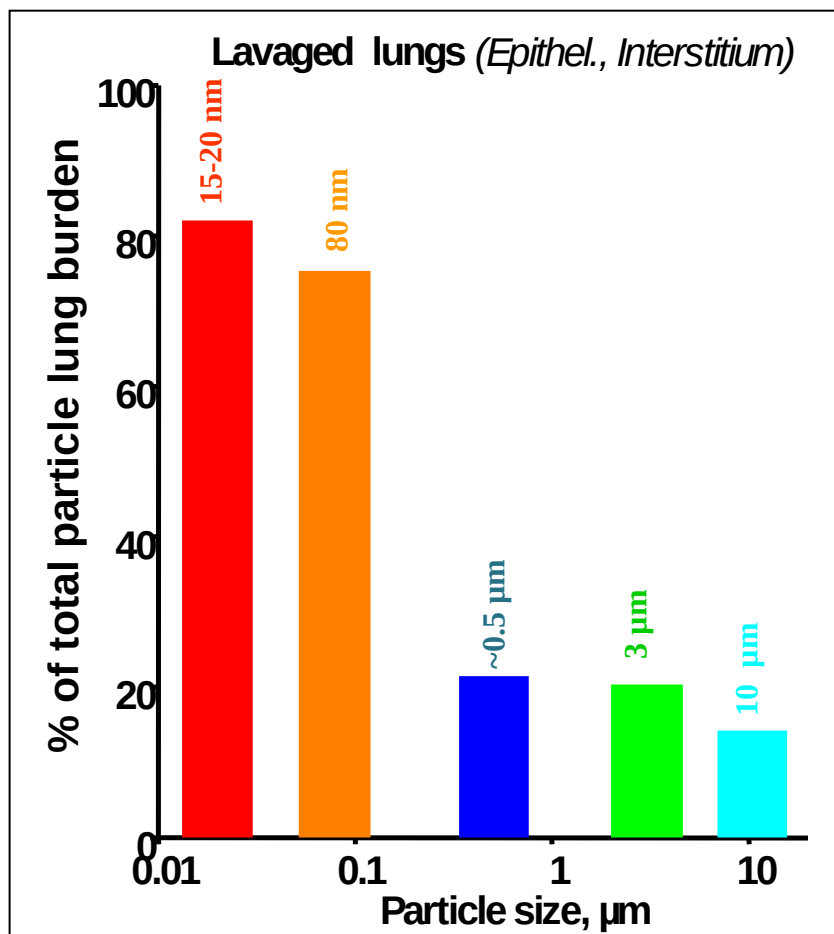
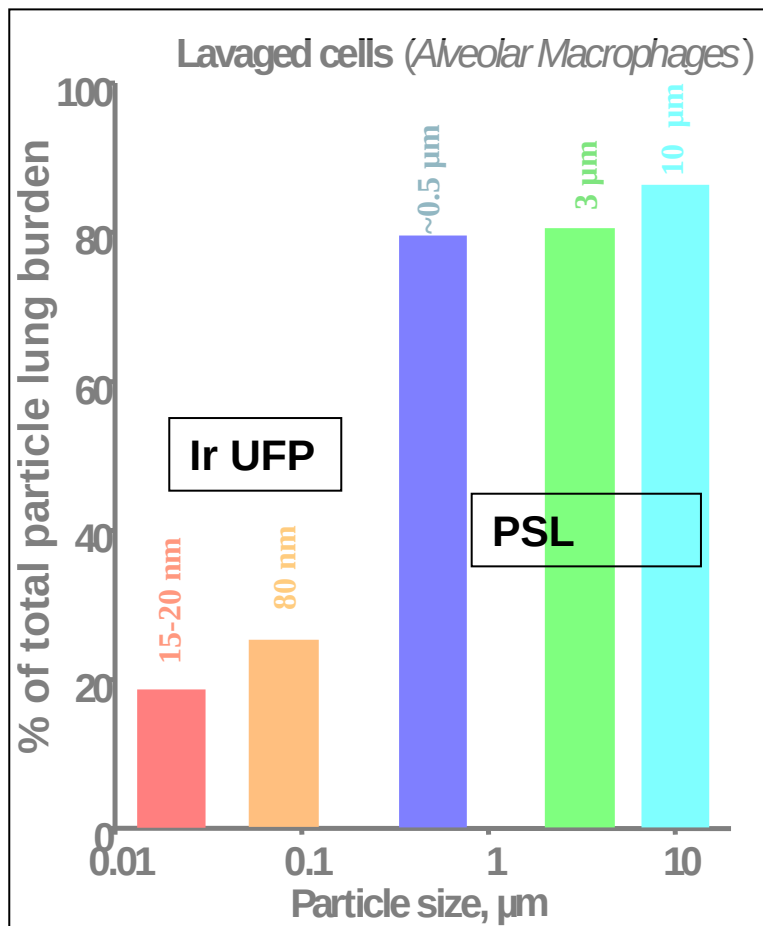
FIGURE 3. Deposition locations on the 3D airway surface for three particle sizes (1, 10, and 30 μm) at steady flow rate of 15 L/min.



- ICRP lung deposition
 - Deposition $\sim f(D_p)$
 - Spatial distribution
 - CFD
-
- Application to nanoparticles still in its infancy

Particle-size dependent retention sites in lungs

Retention of ultrafine, fine and coarse particles in alveolar macrophages of rats determined 24 hrs post-exposure by exhaustive lung lavage



Oberdörster et al., 2001; Kreyling et al., 2002

UFP not accessible to lavage; → relocated into epithelium & interstitium

Assessing the pulmonary toxicity of single-walled carbon nanohorns

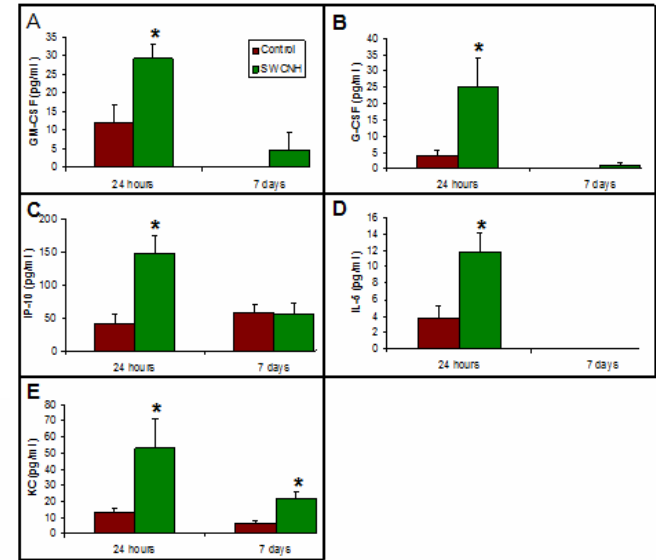
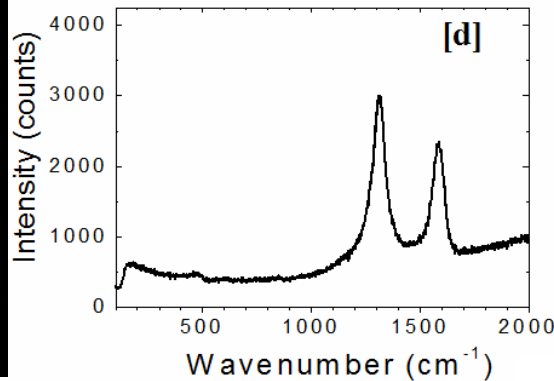
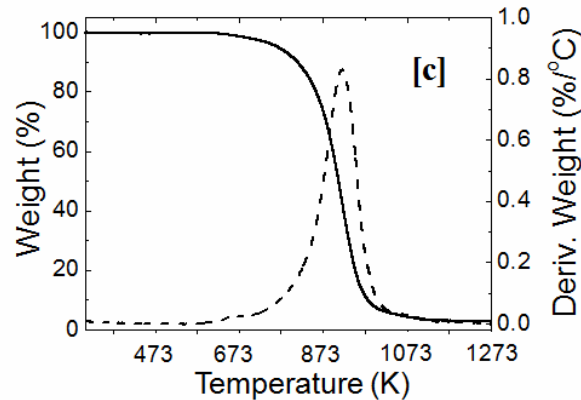
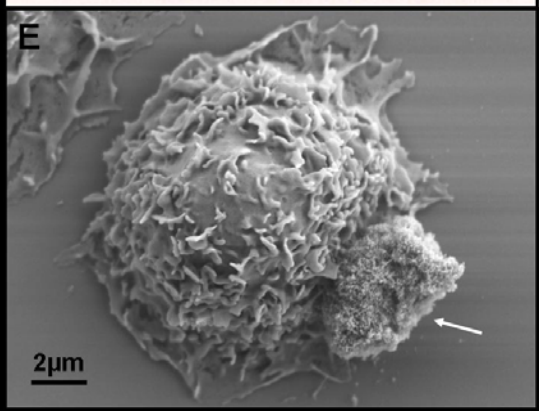
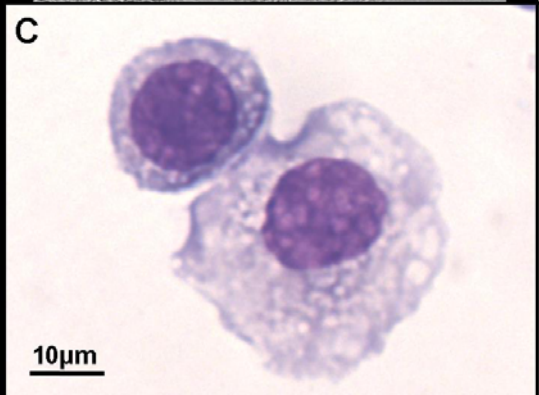
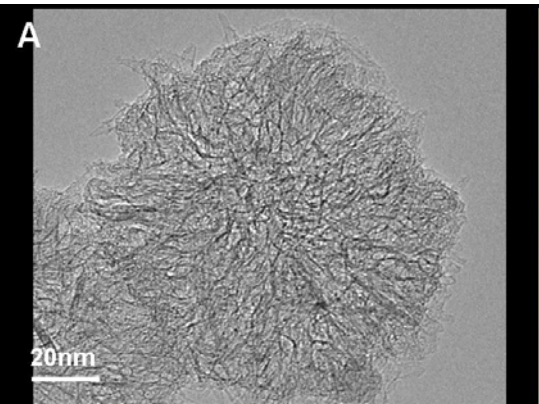
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Abstract

Previous studies have suggested that single-walled carbon nanotubes (SWCNTs) may pose a pulmonary hazard. We investigated the pulmonary toxicity of single-walled carbon nanohorns (SWCNHs), a relatively new carbon-based nanomaterial that is structurally similar to SWCNTs. Mice were exposed to 30 µg of surfactant-suspended SWCNHs or an equal volume of vehicle control by pharyngeal aspiration and sacrificed 24 hours or 7 days post-exposure. Total and differential cell counts and cytokine analysis of bronchoalveolar lavage fluid demonstrated a mild inflammatory response which was mitigated by day 7 post-exposure. Whole lung microarray analysis demonstrated that SWCNH-exposure did not lead to robust changes in gene expression. Finally, histological analysis showed no evidence of granuloma formation or fibrosis following SWCNH aspiration. These combined results suggest that SWCNH is a relatively innocuous nanomaterial when delivered to mice in vivo using aspiration as a delivery mechanism.

Keywords: Single-walled carbon nanohorns, nanotoxicology, aspiration, inflammatory



- Pure carbon produced by ORNL/ALSP (no metals)
- PEG Surface-decorated for mice exposure by pharyngeal aspiration (30 µg/mouse)
- Carbon agglomerate core (~80 nm) with embedded nanohorns (10-20nmL x 2-5 nm dia.)
- 500-5000 singlet horns per agglomerate core
- Applications: Pharma, energy storage, diagnostics, ...

Not all nanoparticles are biologically active!

Gaps and Needs in Monitoring Nanoparticles

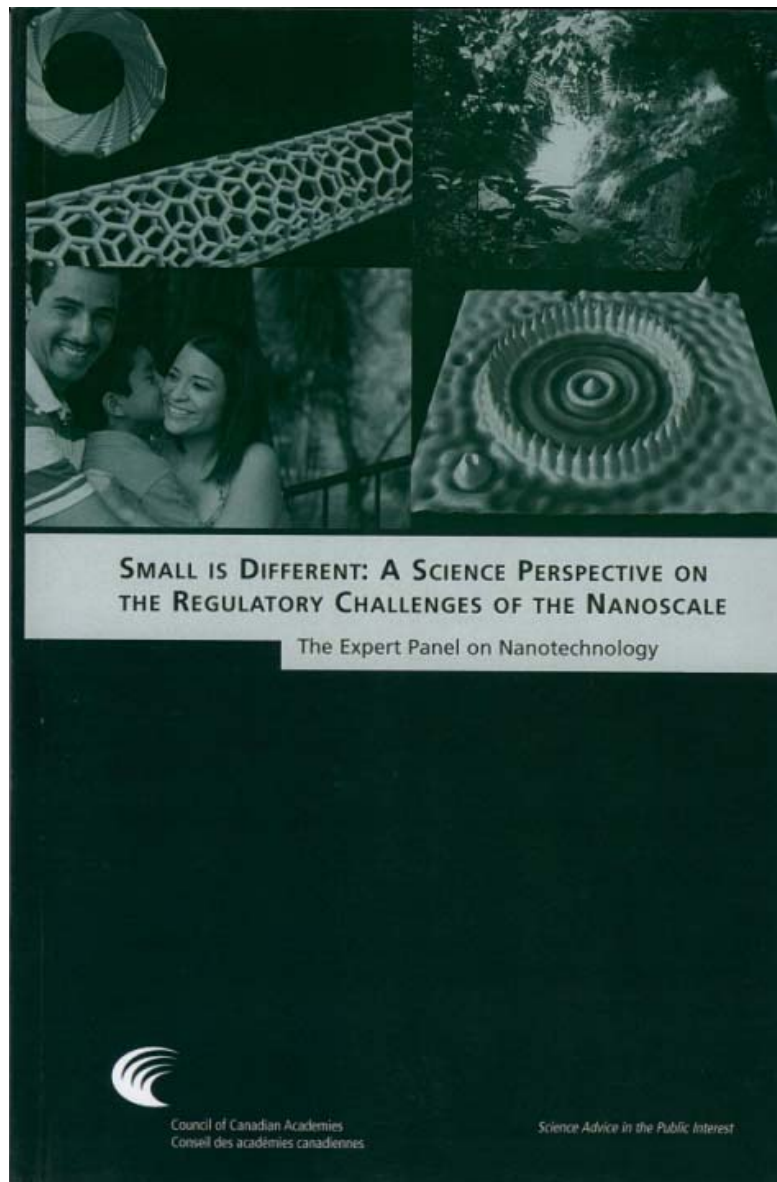
- **Gaps**

- Application specific
- No single method applicable to all cases
- Lack of reference materials

- **Needs**

- Improved understanding of biological sensitivity to individual variables or combination of variables
- Positive detection as engineered nanoparticles
- Improved measurements need to tie with biological responses.

Scientific Publications



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