Research Need 5: Understand Workplace Processes and Factors that Determine Exposure to Nanomaterials

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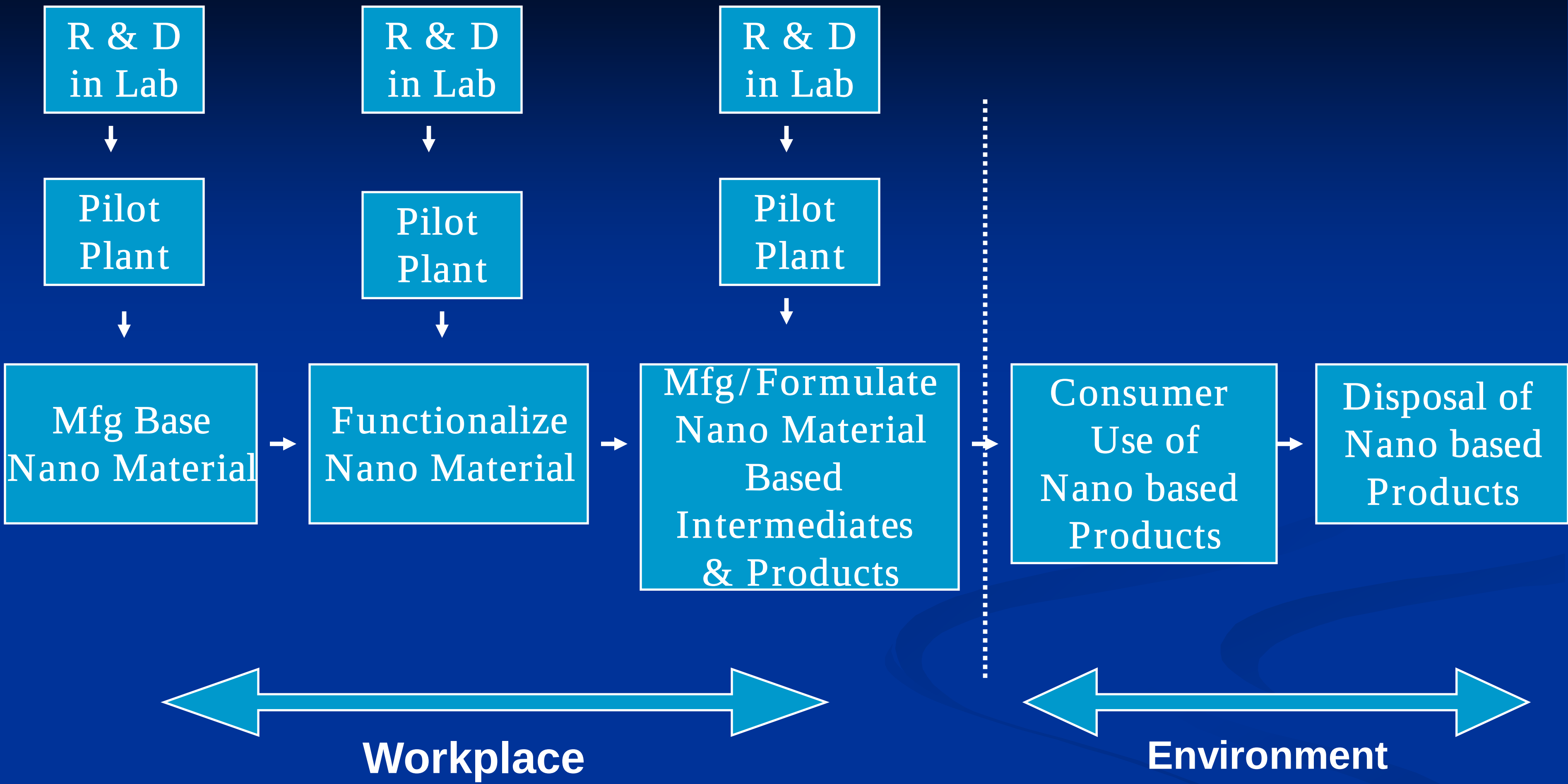
Research Need 5: Understand Workplace Processes and Factors that Determine Exposure to Nanomaterials

- Develop exposure classification of nanomaterials
- Develop exposure classification of processes
- Develop predictive models of workplace exposure

TABLE 4-1 NNI Evaluation of Federal Grant Awards in FY 2006 That Are Directly Relevant to EHS Issues

Category	No. Projects	$ Invested (Millions), FY 2006
Instrumentation, Metrology, and Analytical Methods	78	26.6
Human Health	100	24.1
Environment	49	12.7
Human and Environmental Exposure Assessment	5	1.1 <2%
Risk Management Methods	14	3.3
TOTAL	246	67.8

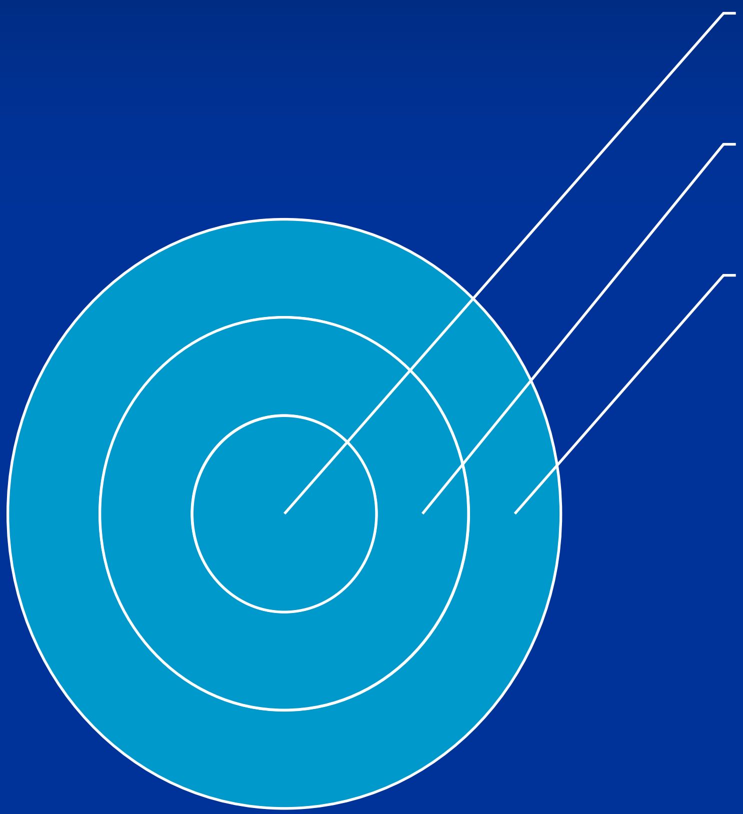
Source: NNI 2008.



Sectors with Potential Risk from Engineered Nanomaterial (NM) Use

How to Classify Workplace Processes and Materials along with Factors that Determine Exposure to NM?

Levels of Potential Exposure Determinants for Nanomaterials



Micro Level:
Differences between operations or tasks using NM

Mid Level: differences between organizations by NM industry sector or by NM used

Macro Level:
differences across all NM industry sectors or product types

Macro Level Determinants of Potential NM Exposure

Data from across all NM industry sectors or general NM Product sectors based on *ICON Survey of Current Practices in the Nanotechnology Workplace, 2006*

- Type of activity
  - 42% R & D
  - 27% Mfg Nano Material
  - 19% Mfg products (plastics, textiles, ceramics)
- # Employees
  - 47% of organizations have < 50 employees
- Length of experience with material
  - 56% of organizations < 10 years old
  - 86% have worked with nanomaterials for < 10 years
- Type of Material Used

6 Basic Nanomaterial Categories (ICON, 2008)

- **Oxides:** TiO_2, ZnO, CeO_2, Fe_3O_4 MnO_2, SiO_2
- **Metals:** Ag, Co, Ni, Fe, Pt, Pd, Rh, Au, Al, Cu
- **Carbon Based Nanoparticles:** Nanotubes (single, double & multiwall); Nanohorns; Fullerenes (bucky ball); Nanofibers; Graphene sheets;Carbon black
- **Quantum Dots:** fluorescent crystalline semiconductor NM
- **Macromolecules:** branched polymeric organic molecules
- **Self-assembled:** lipids, metal oxides, organic molecules self organize due to inherent physical properties.

- **What are commonly used NM ?** (ICON Survey 2006)
  - 45% Metal oxides &/or pure metals
  - 45% CNT + 19% Fullerenes + 19% other carbon NM
  - 30% Colloidal dispersions (unspecified)
  - 14% Quantum dots
  - 20% Dendrimers or polymers

Macro Level Determinants of Potential NM Exposure

SUMMARY

- No data linking macro level determinants to actual exposure measurements

- Using Frequency of Reporting from ICON 2008 Survey to prioritize targets for exposure evaluation:
  - R & D & Base NM Manufacturers
  - Small (< 50 employees) and young (< 10 years old) organizations
  - Use CNT/fullerenes or metal oxides/pure metals

- Problem with this approach is that it does not include relative toxicity as a priority

- Does not cover other basic NM groups identified by ICON

Mid Level Determinants of Potential NM Exposure

- Data to compare exposures between organizations
  - Based on NM Industry sector (R & D; Mfg of NMs; Mfg of NM Products)
  - Based on NM material used (Products: Composites, Textiles, Coatings or base NM)

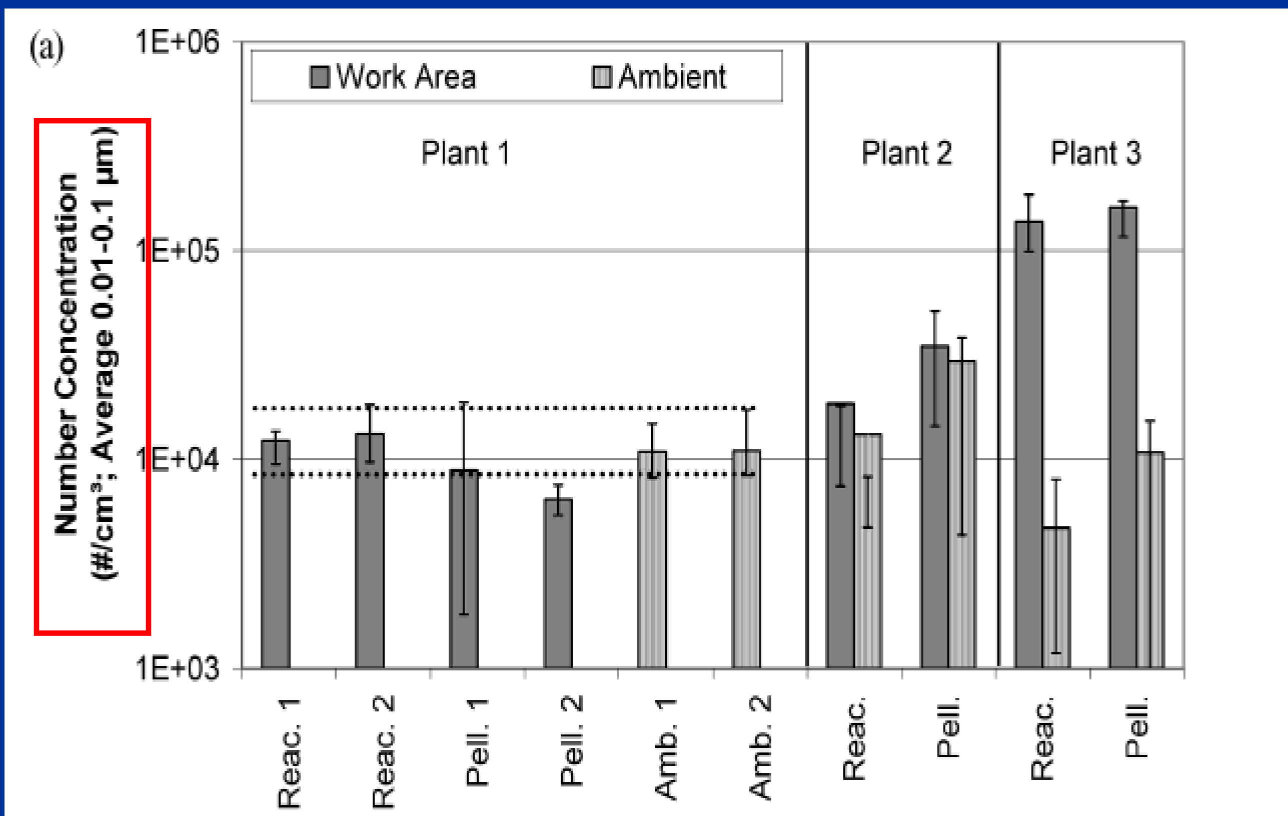
- Potential determinants:
  - Type of Product
  - Rate/volume of production
  - Company demographics (profitability, public/private)
  - Descriptors of physical worksite (size and age)
  - Rating of worksite H & S program
  - Geographic Location (seasonal factors)
  - Target sales audience

- Only 1 study to date

Carbon Black Plants

- Carbon Black Reactors produce particles 10-100nm
- Pelletizing & Packaging of nano carbon black
- Repeat sampling of same process to get Avg and 25-75%ile

ant



Plant 1: No in/out diff

Plant 2 No in/out diff
but higher than plant 1 due to nearby traffic?

Plant 3: Signif in/out diff
high OC level so other production leaks?

Kuhlbusch et al
JOEH 2006

Micro Level Potential Exposure Determinants

- Micro level starts at Job or Operation
- Worker Daily Job/Operation Exposure %

  3 (Task Intensity x Duration)
- Looks at Tasks within the Operation

NIOSH Draft Guidance on Nanotechnology, 20

Potential determinants of welding fume exposures

Work Environment factors: temperature, humidity, ventilation measures: cross current, capture velocity, face velocity, capture distance

Work practices- worker distance from arc, plume direction, workers posture

Process factors voltage, amperage, type of welding technique

Material factors – base metal, rod diameter, rod type, number of rods used.

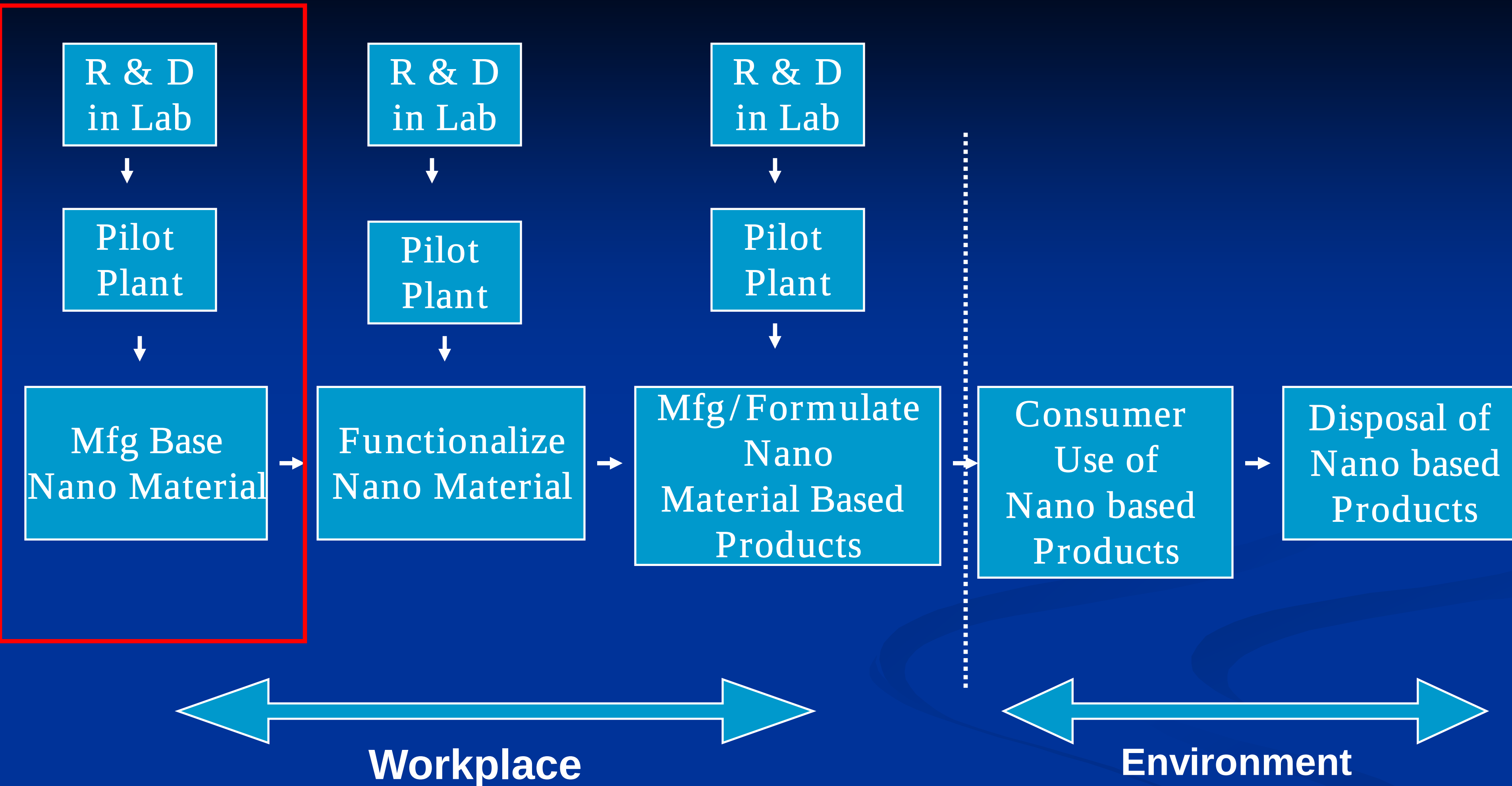
Song et al, 2006

Multiple Regression Model for Total Welding Fumes

$$\text{Ln (Welding Fume Conc)} = b_0 + b_1(\text{Var}_1) + b_2(\text{Var}_2) + .. b_n(\text{Var}_n$$

Variable	β	P-value
Intercept	0.747	0.08
Welders distance from arc (in)	-0.051	0.004
Voltage of welding machine	0.385	0.06
Plume direction (toward/away)	0.728	0.0004
Capture velocity of LEV (fpm)	-0.401	0.05
Indoor humidity (%RH)	0.011	0.035

Model: $R^2 = 0.50$, p-value = <.0001



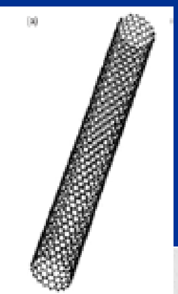
Points of Potential Risk/Exposure with Nanomaterial Use

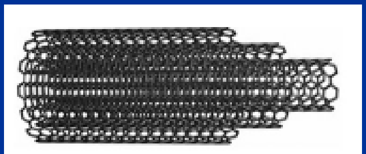
What do we know about potential exposure determinants in the NM environment?

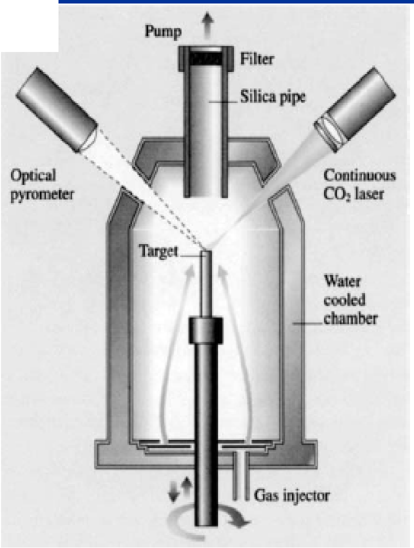
Material Process Factors Environmental Factors Individual Factors

Manufacturing of Base Nanomaterials

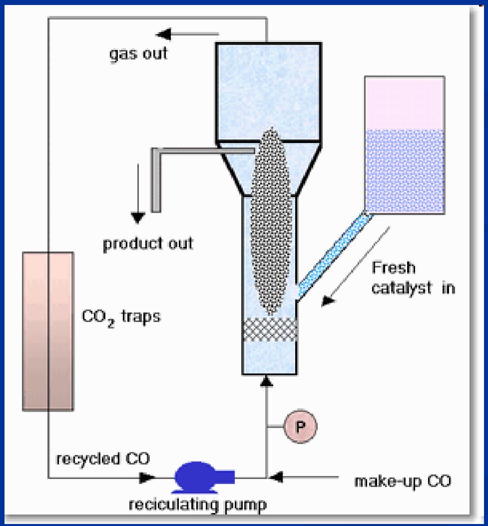
- NM's are produced in two ways:
  - Top down: larger bulk material broken into nano size via mechanical, chemical or other energy
  - Bottom up: Synthesis from atomic or molecular sub-components through chemical reactions



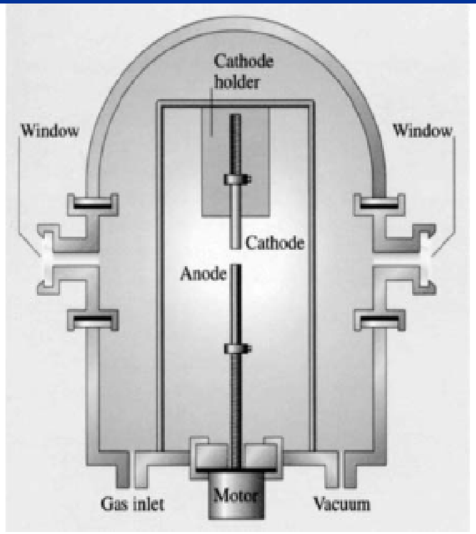




Laser Ablation



Chemical Vapor Deposition (CVD)



Arc Discharge (Electro-Explosive)

Tasks with Potential Exposure to NM During Manufacturing Base Material?

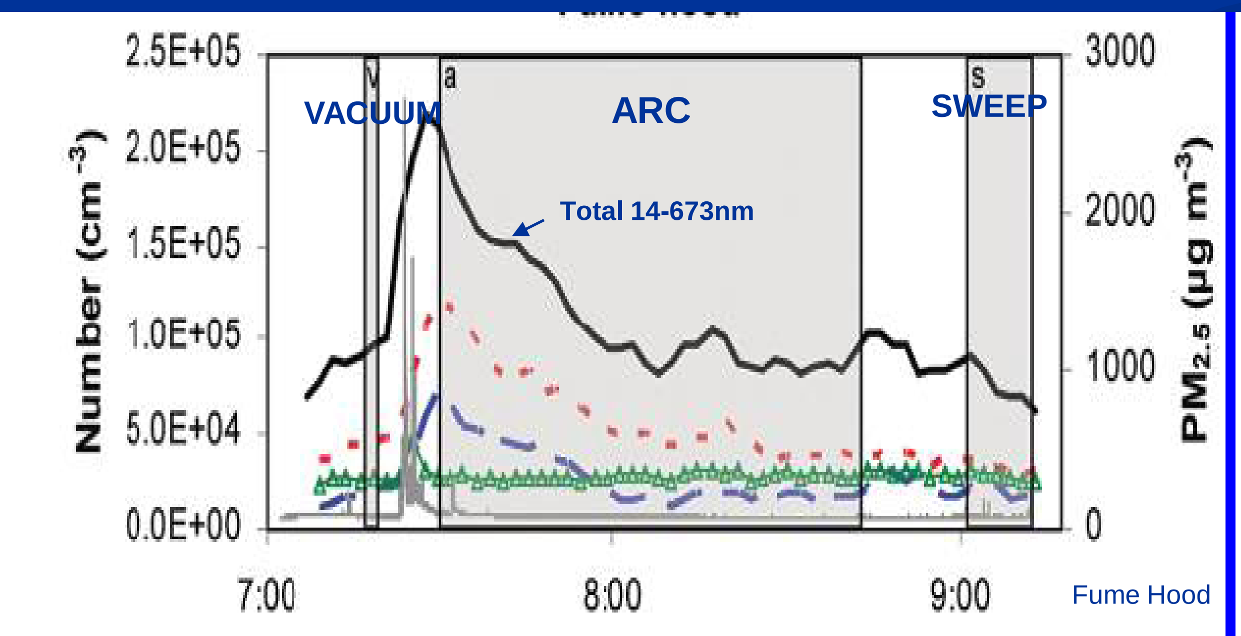
- Setting up and running reactors
- Unloading reactors
- Finish processing of NM product (drying etc)
- Maintenance and cleaning of reactors
- Packaging and shipping of final product
- Accidental spills
- Waste product handling

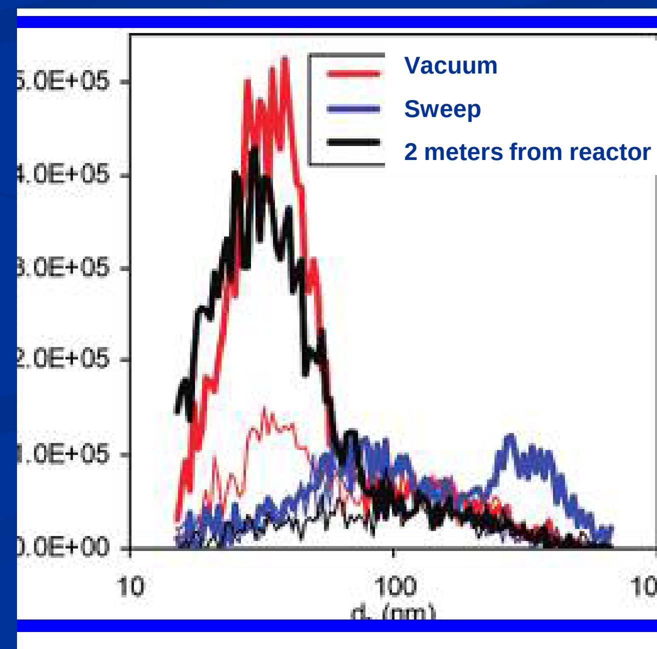
In the semiconductor industry typical maintenance & cleaning tasks had exposures 70-95 times higher than typical operation tasks.

Woskie et al, AJIM 1995

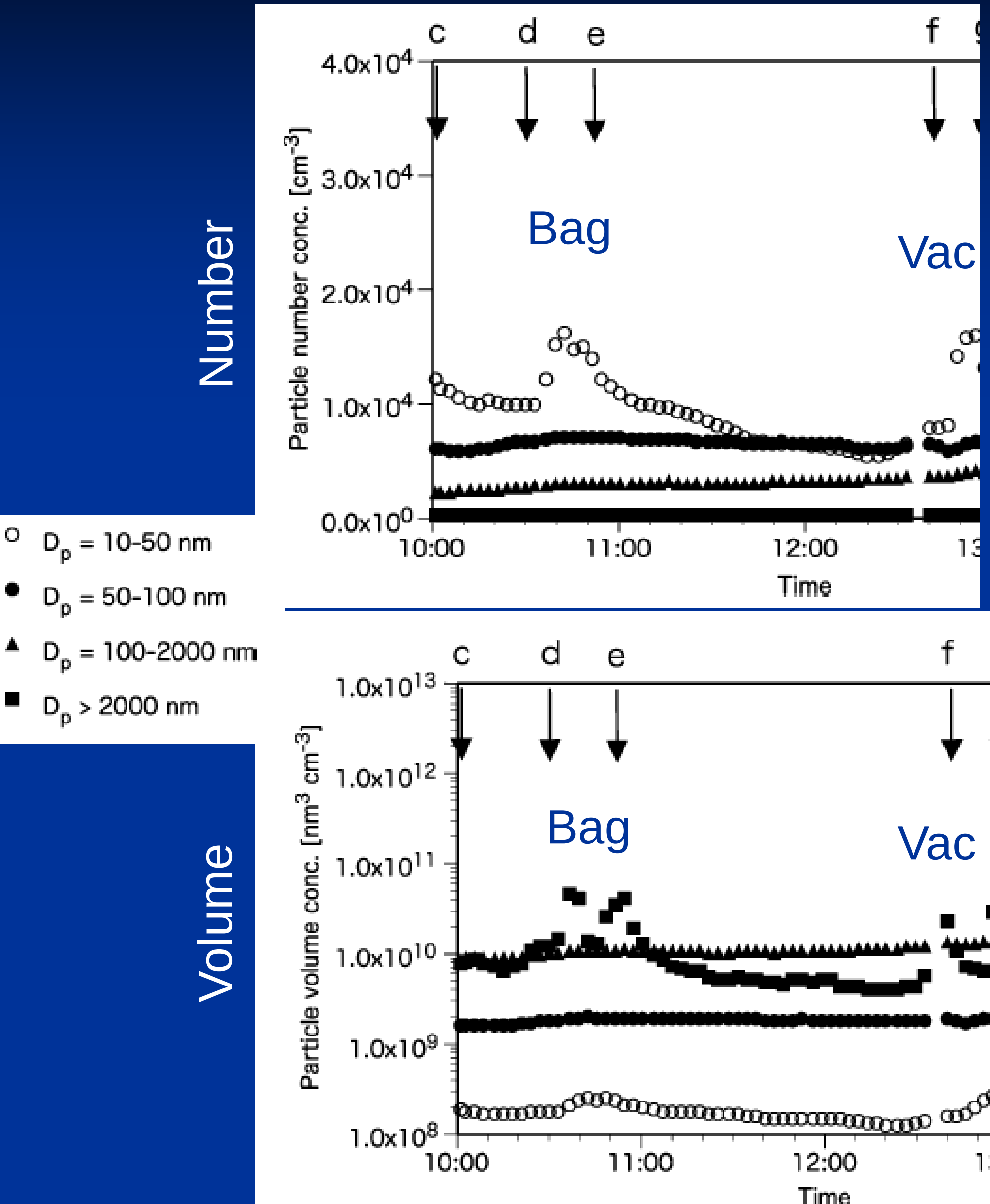
Fullerene Manufacturer (Yeganeh et al EST, 2008)

- Monitored 12 production runs. Each includes:
- Vacuum Maintenance: reactors are vacuumed to remove residual NM from the reactor chamber & inside the ventilated reactor enclosure.
- Arc setup & reaction: tech places graphite rods inside the reactor, seals it. Electric arc across the rods produces NM
- Sweeping to remove Product: tech opens the reactor & using a scoop and a brush, sweeps out NM into a jar.
  - Particle counts generally low for Arc, but higher for Vacuum & Sweep
  - Particle size small with vacuum but larger for sweep





Fullerene Post-Production Tasks

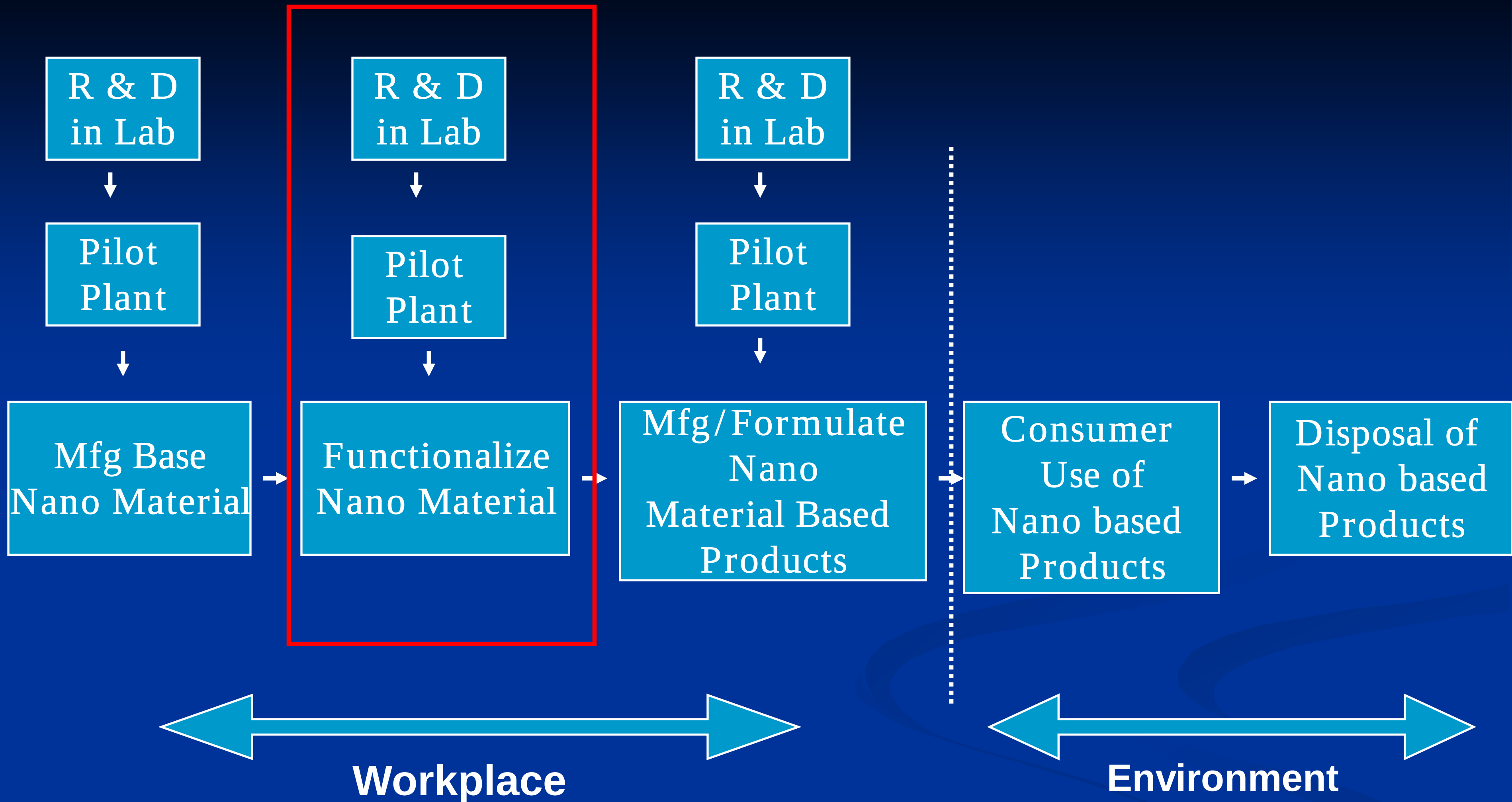


- Fullerene production is in a closed system so no exposure during normal operation
- Bagging dried material
  - C= Indoor air during non-work period
  - D= Bagging = removal of fullerene from storage tank and weighing
  - E = End bagging workers leave room
  - F= Use Vacuum cleaner to remove dust from floor
- Agglomerated NP could be hazard if inhaled

Fujitani et al JOEH 2008

Manufacturing Base Nanomaterials

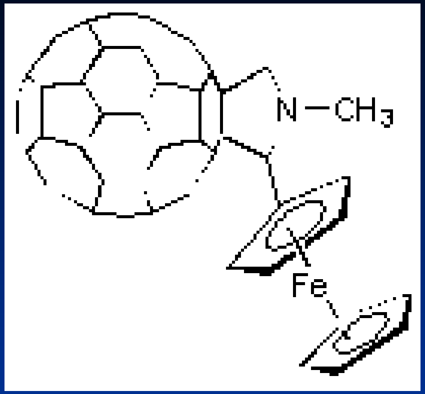
- Summary
  - Leakage of reactors (N)(2)
  - Unloading reactors (Y)(1)
  - Finish processing of NM product (drying etc)
    - Kuhlbusch et al found pelletizer exposures in 1 plant higher possibly due to leaks, especially in the seals of dryer adjacent to pelletizer
  - Maintenance and cleaning of reactors (Y)(1)
  - Packaging and shipping of final product (Y)(2)
  - Accidental spills
  - Waste product handling
- All data to date on Carbon based NM
- None on the other 5 categories of NM

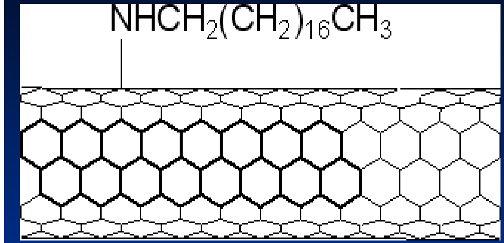


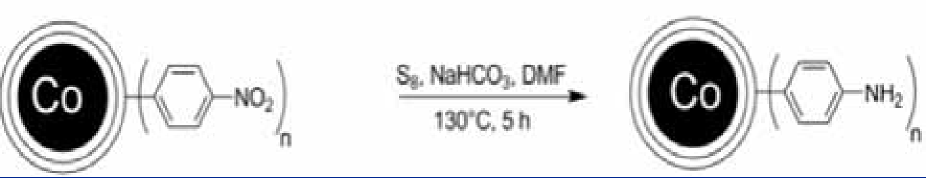
Points of Potential Risk/Exposure with Nanomaterial Use

Material | Process Factors | Environmental Factors | Individual Factors

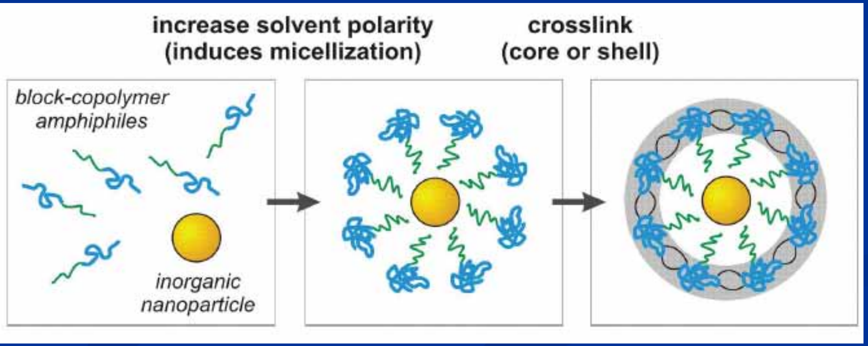
Functionalized Nanomaterials

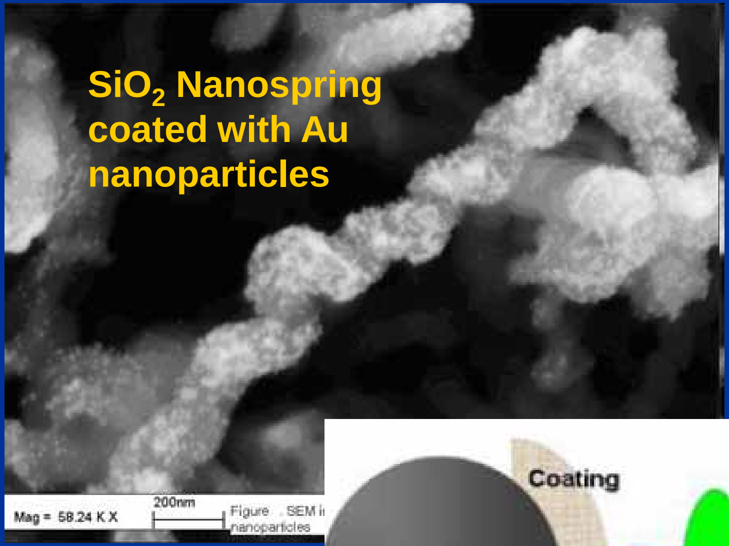




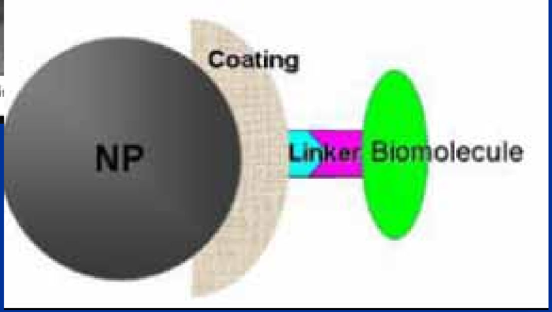


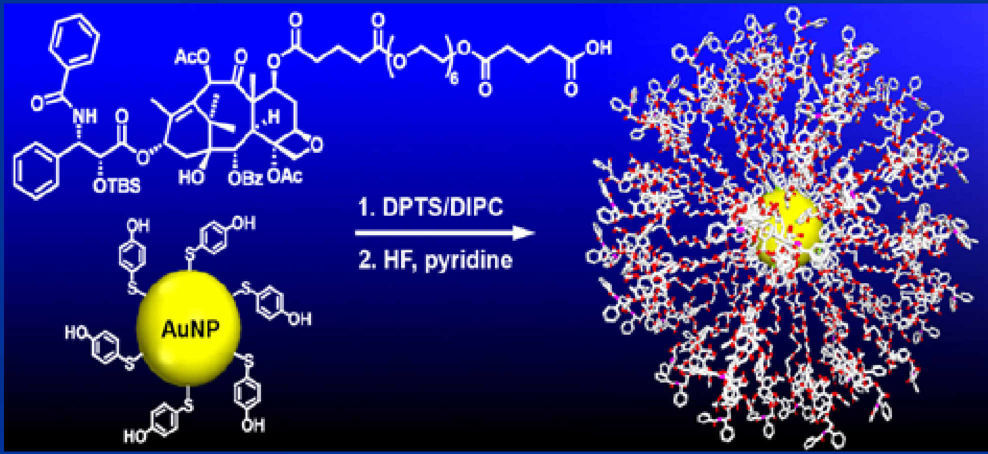
Carbon Coated Cobalt Nanoparticle Nanomagnets





SiO_2 Nanospring coated with Au nanoparticles





Taxol functionalized Gold NP for Cancer Treatment

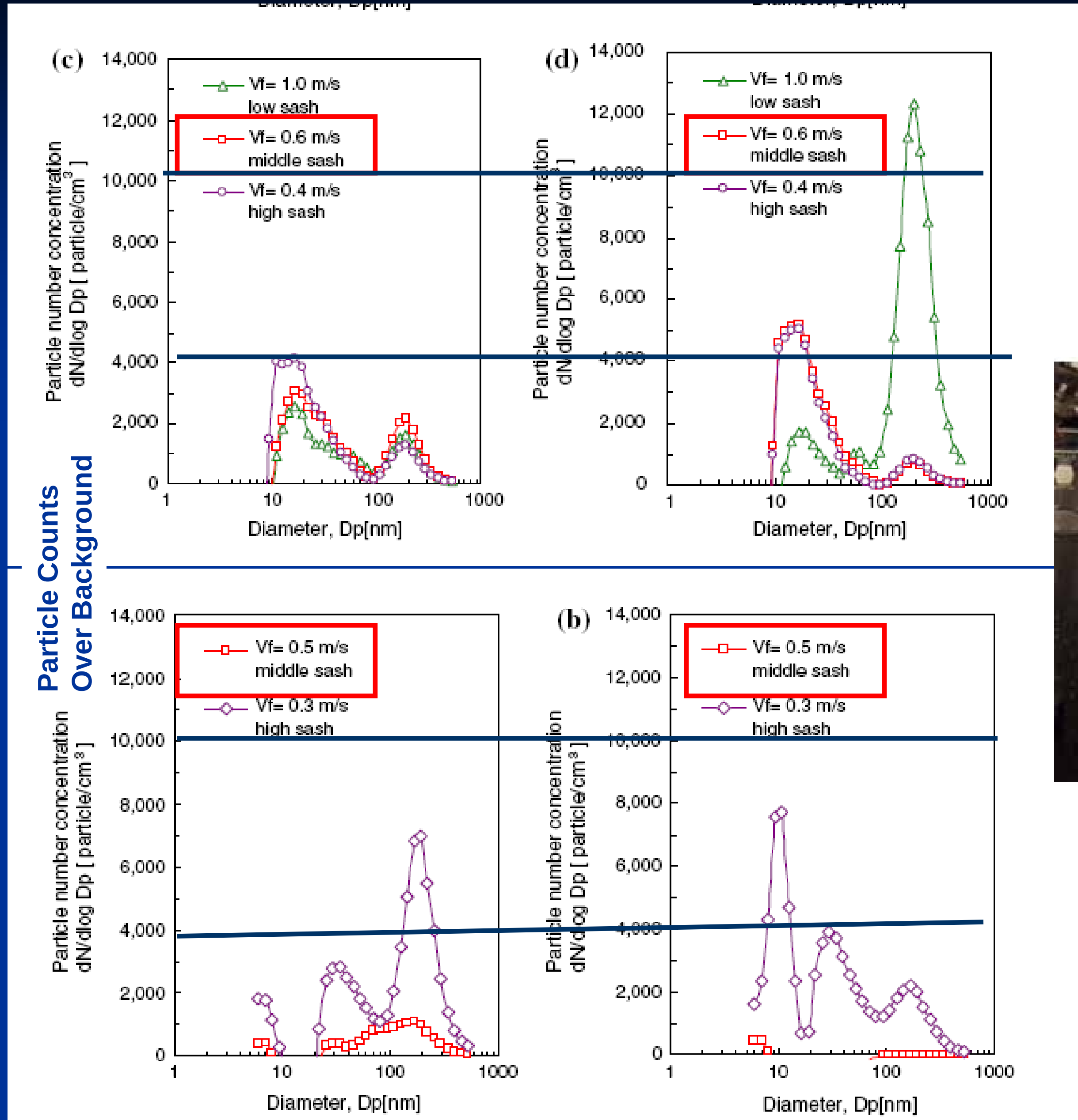
Functionalizing Nanomaterials

- Much of this is R & D work in laboratory settings.
- Significant potential for personal contact
- Tasks of concern include
  - Mixing and pouring of nanomaterials
  - Cleaning apparatus
  - Weighing
  - Preparation for QA/QC testing
- ICON (2008) reports only 47% of those handling dry powder use hood

Conventional Hood

Al_2O_3
27-56 nm
Agglomerates
~ 200nm
100g

Transfer

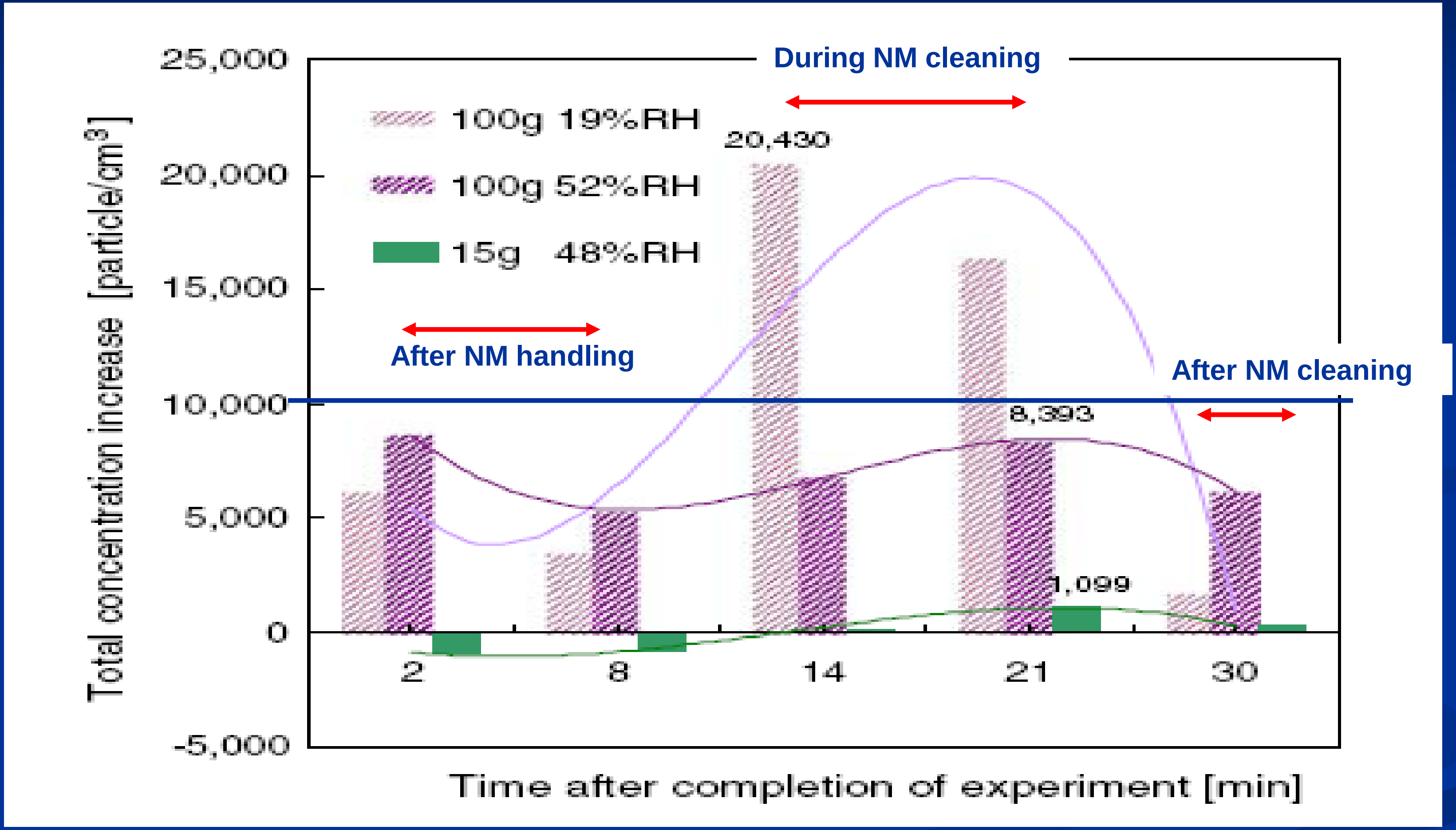


Pour

Bypass Hood

Tsai et al, J Nanopart Res, 2009

NM Use in Lab Hoods



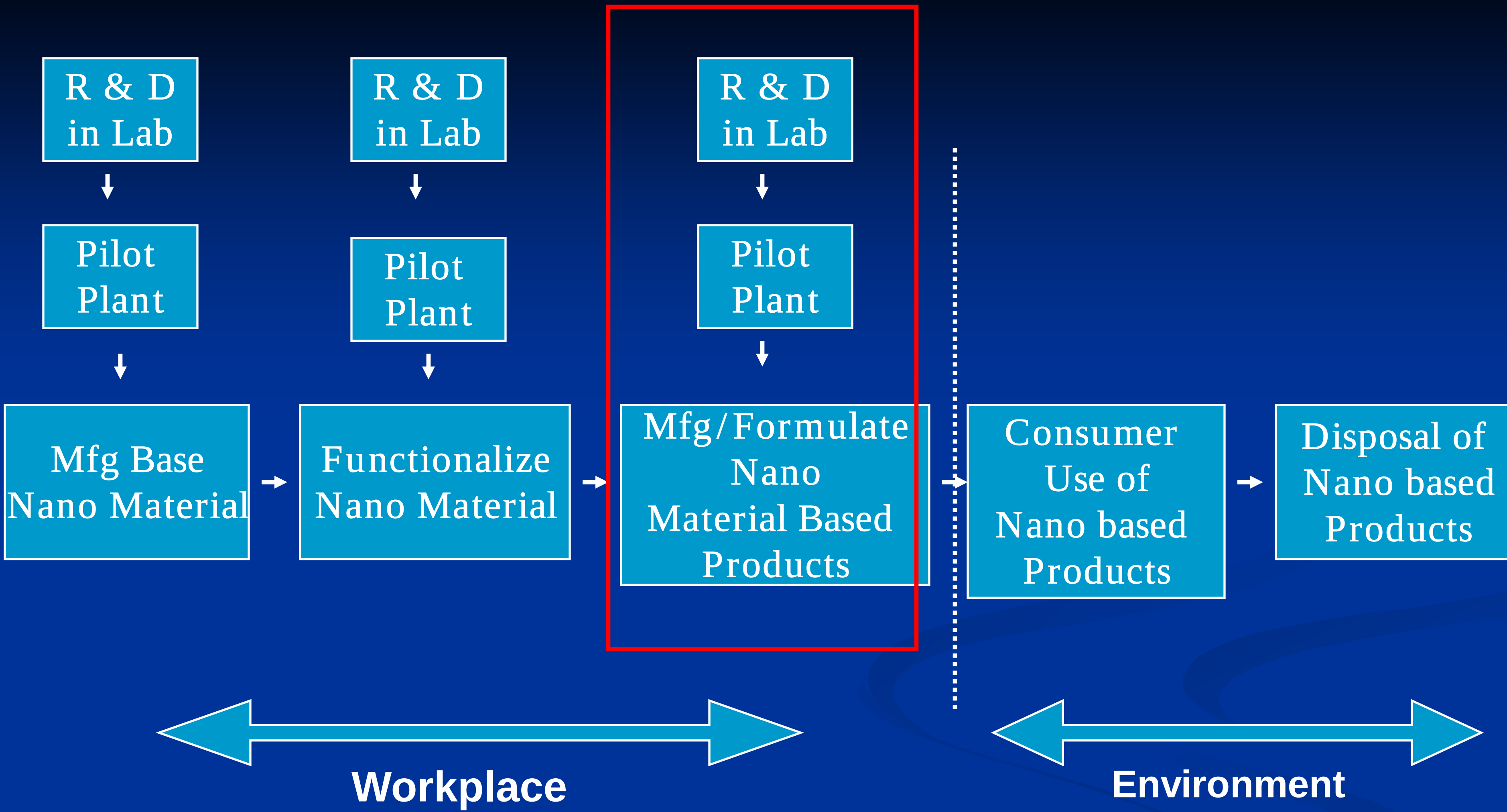
Concentration 1m outside conventional hood after handling NM and during cleaning spilled NM inside hood

Tsai et al, J Nanopart Res, 2009

Functionalized Nanomaterials

Summary:

- We know virtually nothing about exposures during these tasks
  - Transferring and Weighing NM
  - Mixing and pouring of nanomaterials
  - Sonicating dispersions
  - Cleaning apparatus
  - Preparation for QA/QC testing
- ICON report says 23% of organizations used NM as a dry powder only; 37% use NM as a dry powder and in a suspension
- The types of functionalized NM are vast so coordination with toxicologists is needed to target those of greatest concern.
- New hood designs (air curtain) should be evaluated
- The role of thermal load and other NM tasks within hoods needs to be tested.



Points of Potential Risk/Exposure with Nanomaterial Use

Material/Process Factors Environmental Factors Individual Factors

Manufacture/Formulate Products Based on Nanomaterials/Composites

- Much of this is R & D work in laboratory settings.
- Significant potential for personal contact
- Tasks of concern include
  - Transfering and weighing NM
  - Mixing and pouring of nanomaterials as part of producing polymer composites
  - Sonication of NM dispersions
  - Running extrusion processes
  - Cleaning apparatus
  - Machining (cut, drill, sand etc) NM containing products

Nanocomposites

CNT-Carbon Hybrid

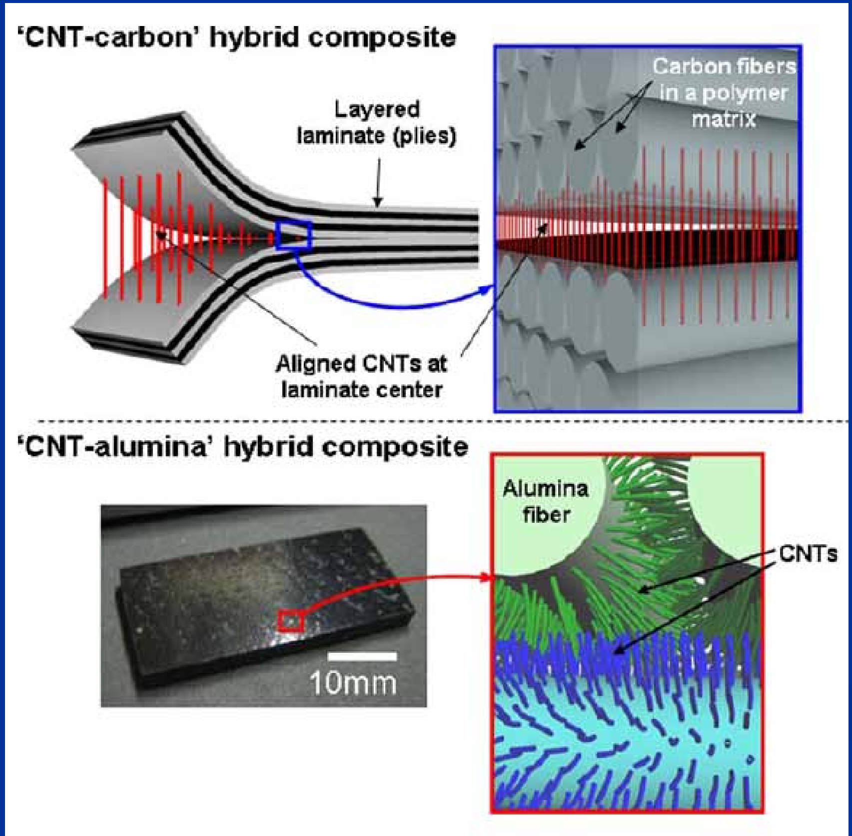
- Carbon nanofibres 8 nm x 150nm on substrate laminated between graphite-epoxy resin matrix

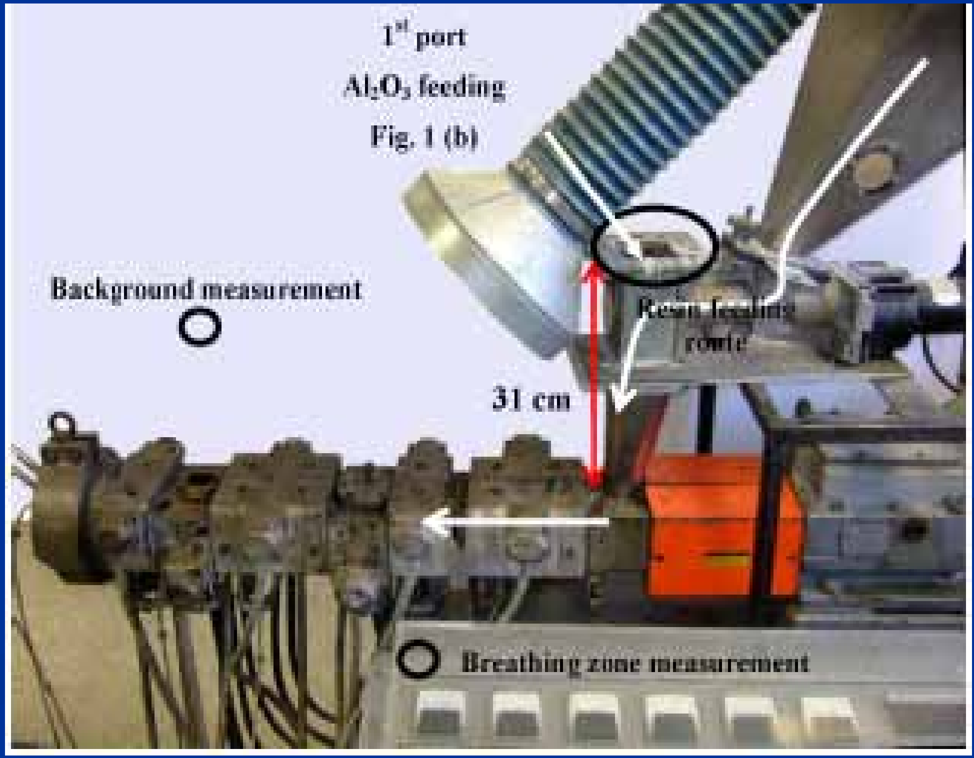
CNT-Alumina Hybrid

- Woven Alumina cloth w/ aligned CNT's on the surface + epoxy resin

Compounding uses

- Extruder > 200º C
- Polymer (ABS or PMMA)
- + Nanoalumina (27-56nm)

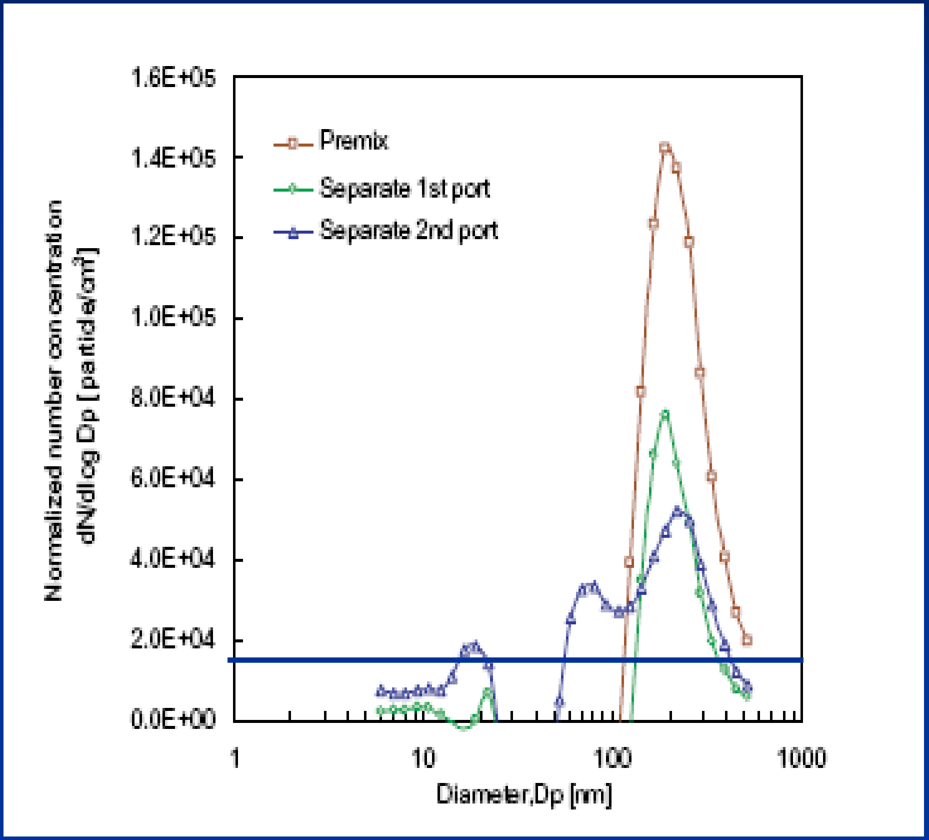


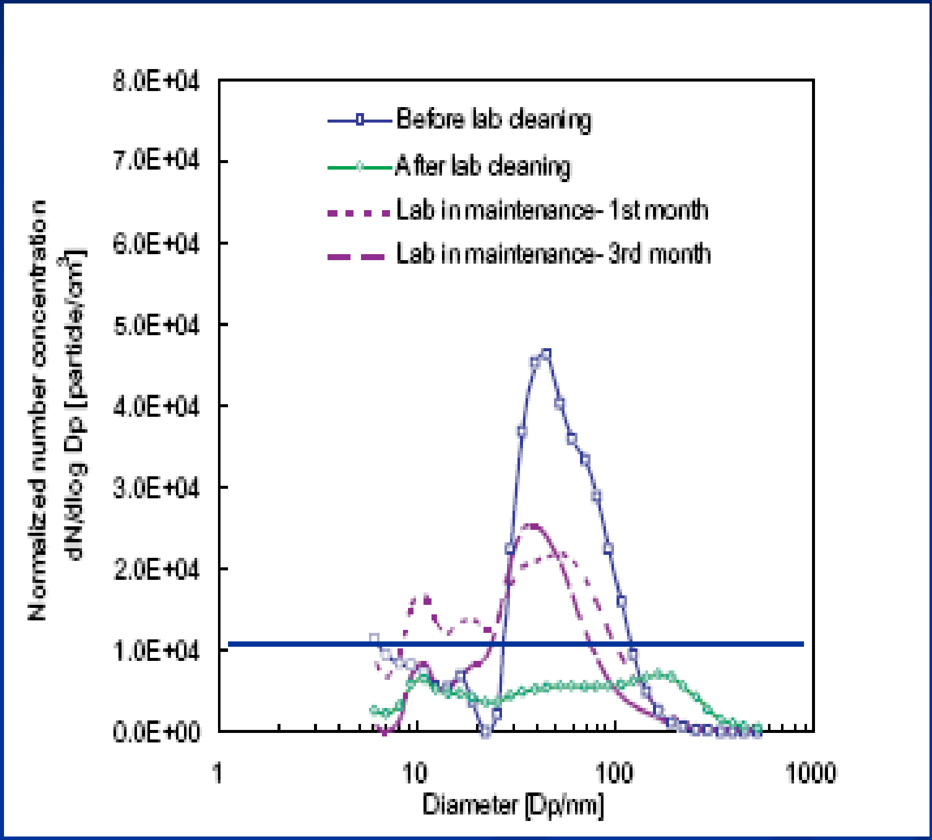


Tsai et al, NANO 2008

What Reduces NP Exposures in Compounding?

How does adding Nano Al_2O_3 via different methods effect exposure?



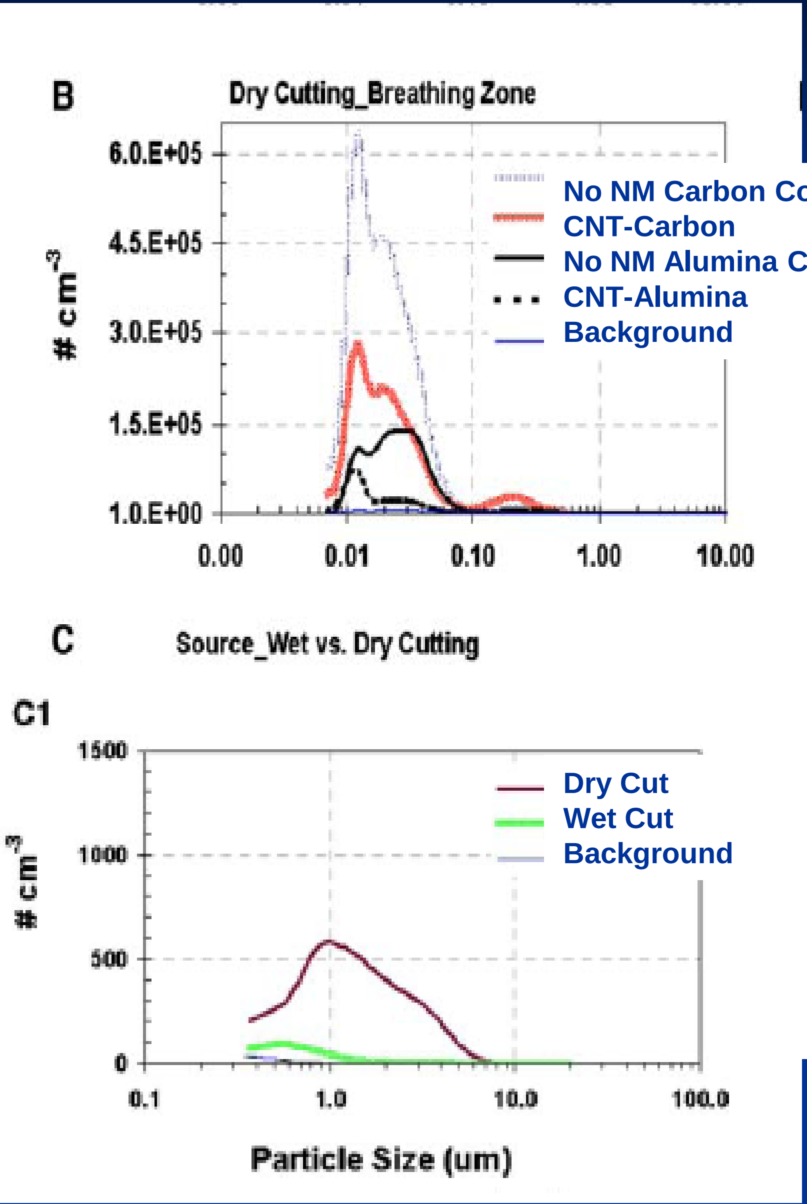


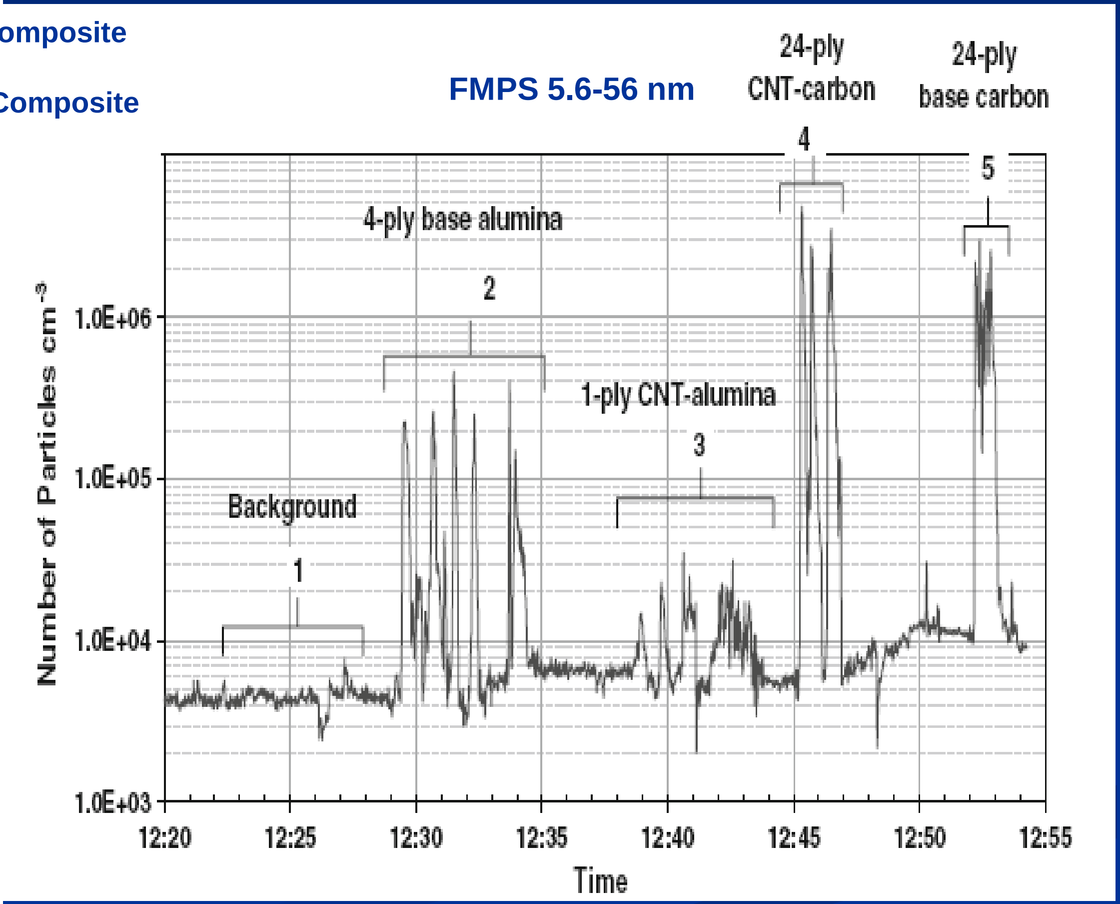
- Background due to polymer fume alone subtracted out
- Premix releases more Al_2O_3 agglomerates
- Premix produces better Al distribution in polymer

- Wash floors & equipment w/ water
- Maintain hygiene

Tsai et al, NANO 2008

Nano Composite Machining

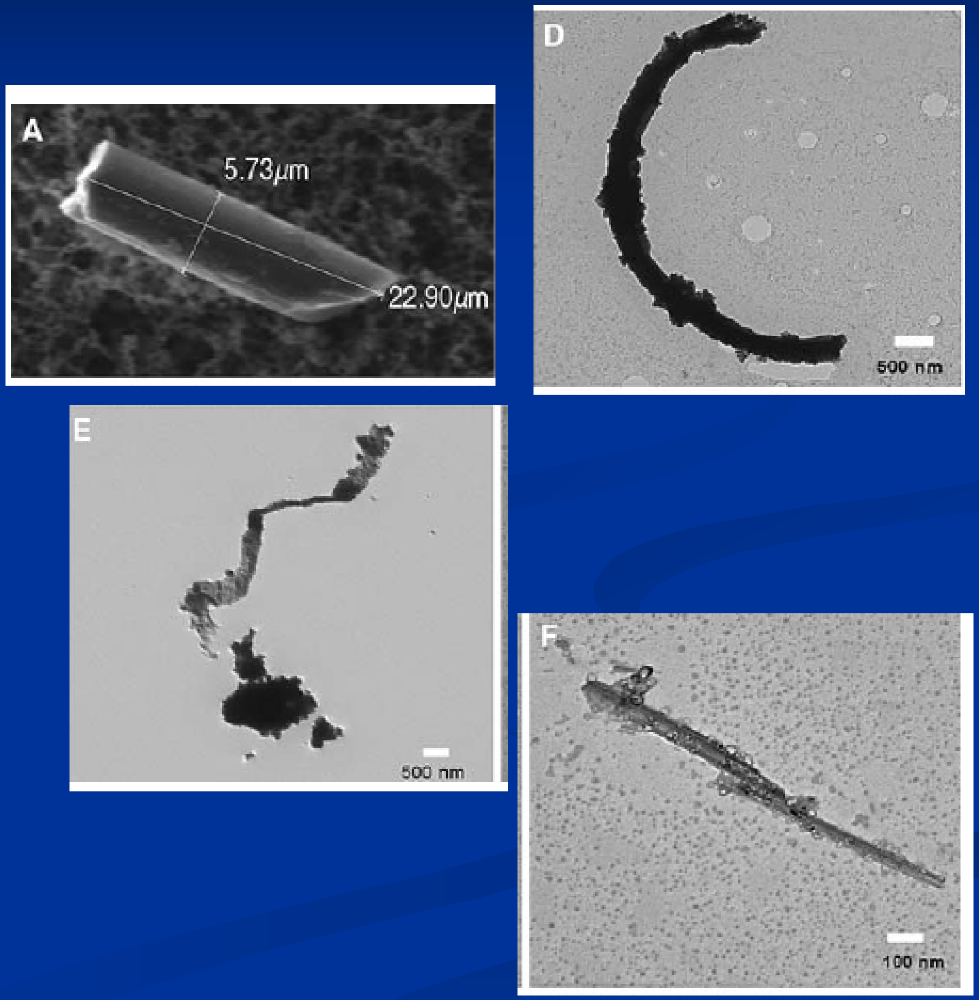




Bello et al, J Nanopart Res 2009

Fiber Production with Machining of Composites

- Cutting of CNT-hybrid composites produced respirable size fibers (though not specifically CNTs)
- Using NIOSH counting rules the concentrations of fibers were: 1.6-3.8 fibers/cm^3
- CNT-Alumina composites produced fewer fibers than CNT-carbon composites
- Han Inhal Tox 2008 also reported finding MWCNT fibers in workplace air samples in a lab setting.



Bello et al, J Nanopart Res 2009

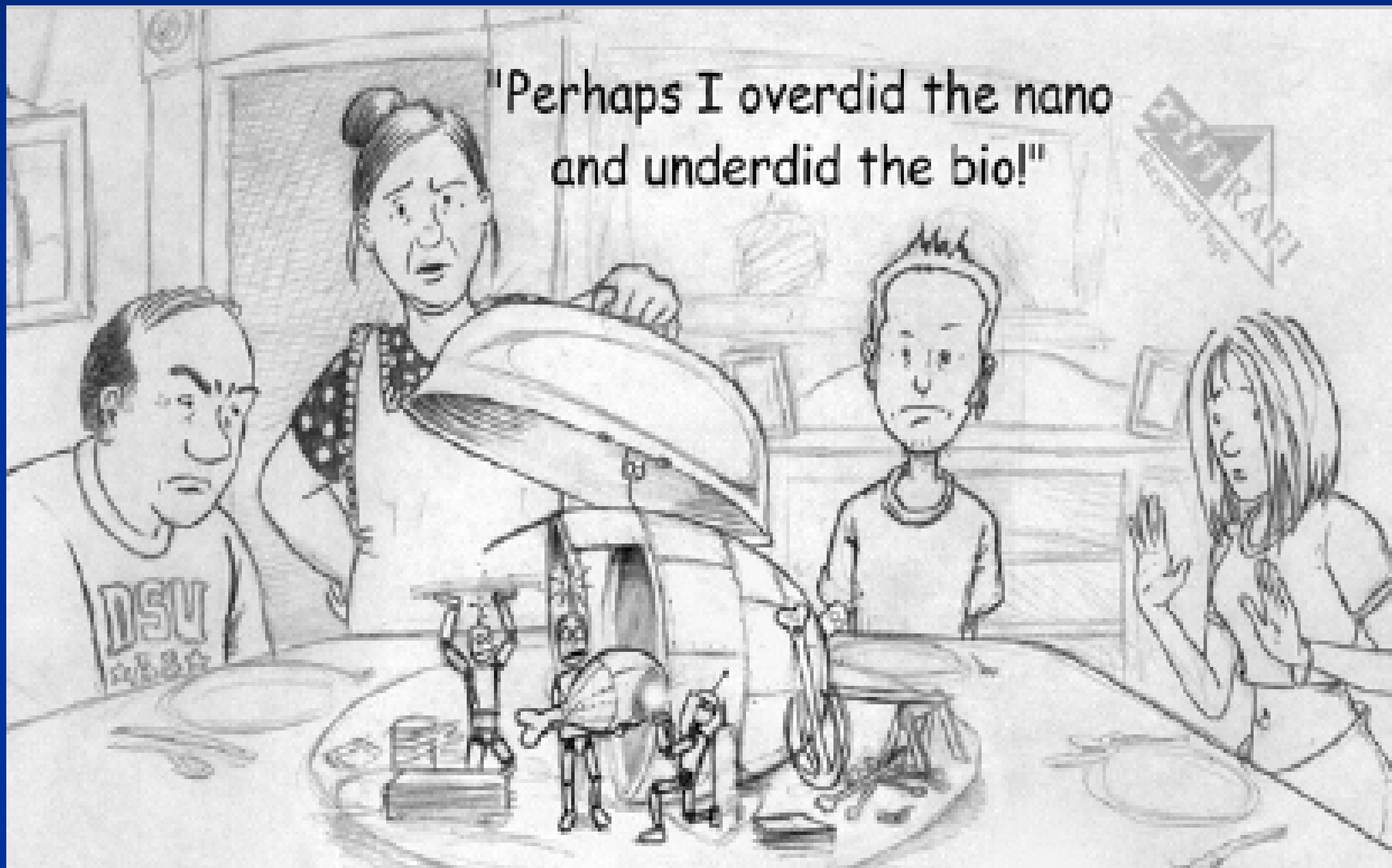
Manufacture/Formulate Products Based on Nanomaterials/Composites

Summary:

- We know very little about exposures during these processes
  - Transfering and weighing NM
  - Mixing and pouring of nanomaterials as part of producing polymer composites
  - Sonication of NM dispersions
  - Running extrusion processes (some)
  - Cleaning apparatus
  - Machining (cut, drill, sand etc) NM containing materials (some)
- All data to date on Carbon nanotubes or nano alumina
- None on the other categories of NM
- Coordination with toxicologists is needed to narrow our targets …..special concern about fibers created during mechanical process with nanotube containing products.

Where do we want to go?

- Need to determine what are the important exposure metrics?
- Need repeat sampling of same tasks within and between organizations
- Need a consistent sampling approach, especially due to the variety of real time particle count size fractions samplers in current use…..
  - Need background measurements near field and far field before AND after task (size distribution and concentration)
  - Need to agree on common size fractions within which to sum concentration data
  - Need to agree on common sampling times to average concentration data over
- Need a targeted list of potential exposure determinants to routinely use for data collection when sampling.
- Need to consider using video exposure monitoring matched with direct reading measurements to allow detailed examination of potential exposure determinants


"Perhaps I overdid the nano
and underdid the bio!"
DSU