

A Comprehensive Environmental Assessment Approach to Making Informed Decisions about Engineered Nanoparticles

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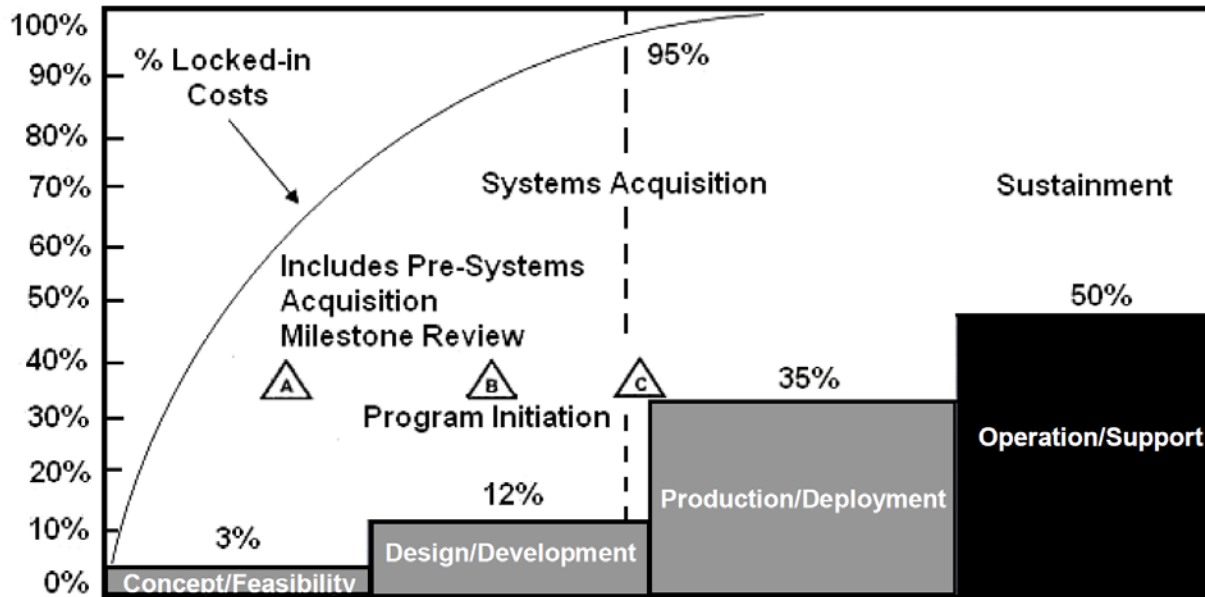
Report Documentation Page

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DoD Materiel Development and Costs



Phase graphics: Robert Cramwell, Sandia National Laboratories, *Ground Vehicle Reliability*, DoD Maintenance Symposium, November 13-16, 2007.

Challenges:

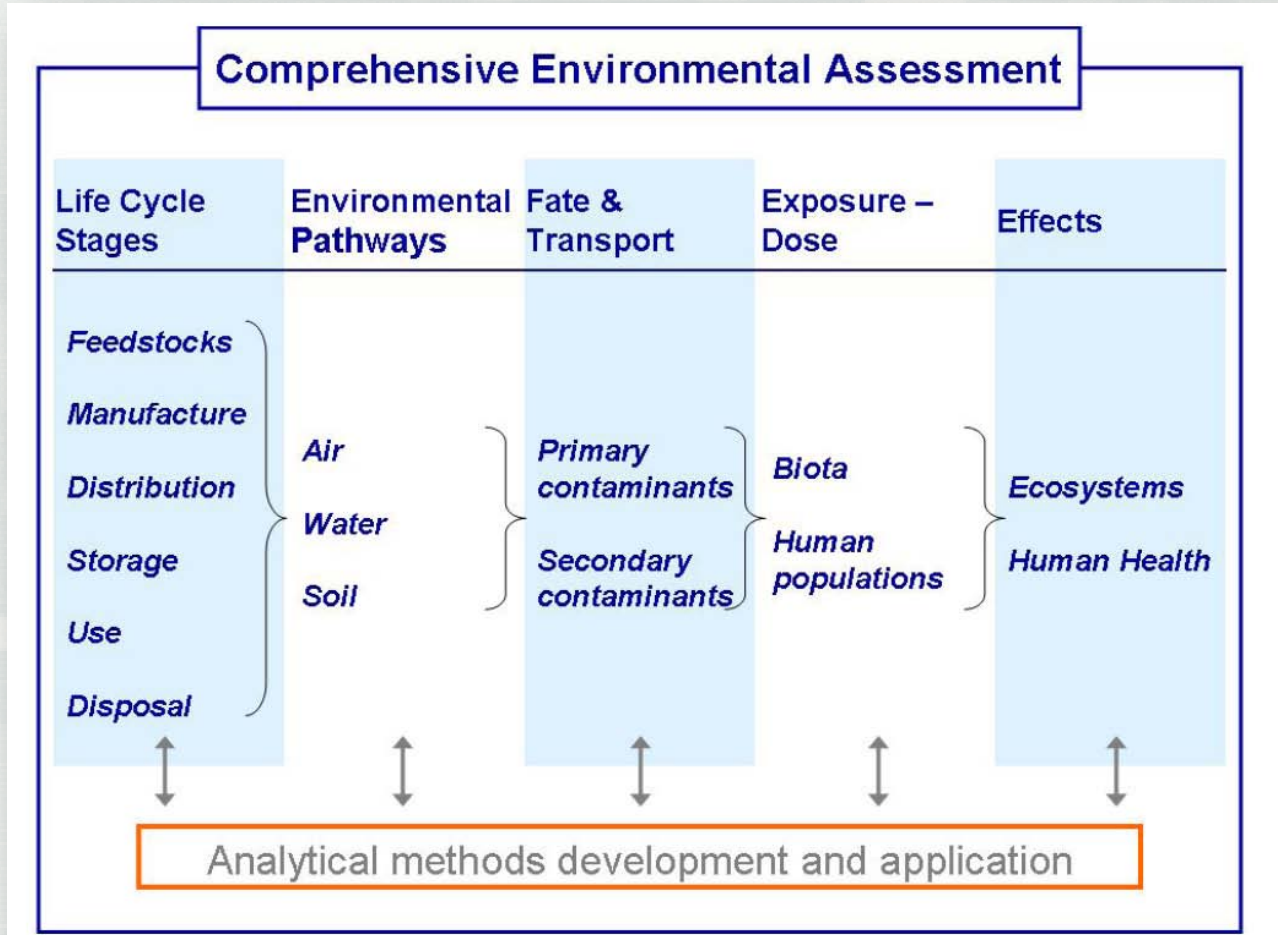
- Regulations (e.g., EU REACH)
- Limited EHS information
- Limited field data & exposure information
- Cost
- Time

- It is estimated that over 85% of the costs of technology occur after systems acquisition



Comprehensive Environmental Assessment (CEA)

Known
Knowns



Known
Unknowns

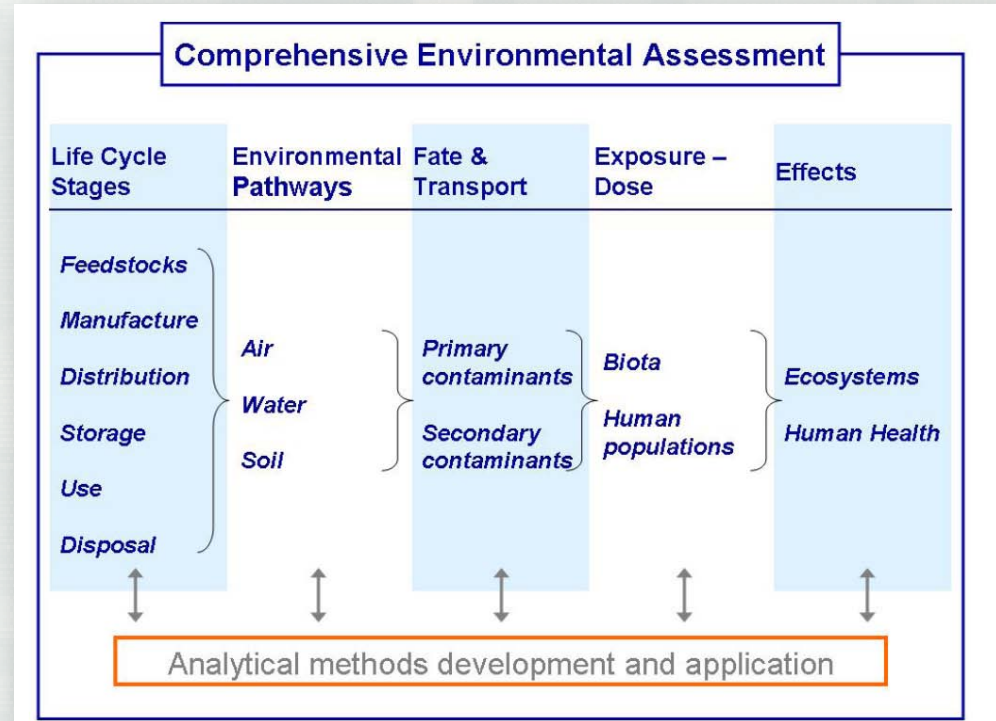
Unknown
Unknowns

Adapted from Davis, 2007



CEA: Lessons Learned with fuel oxygenate MBTE

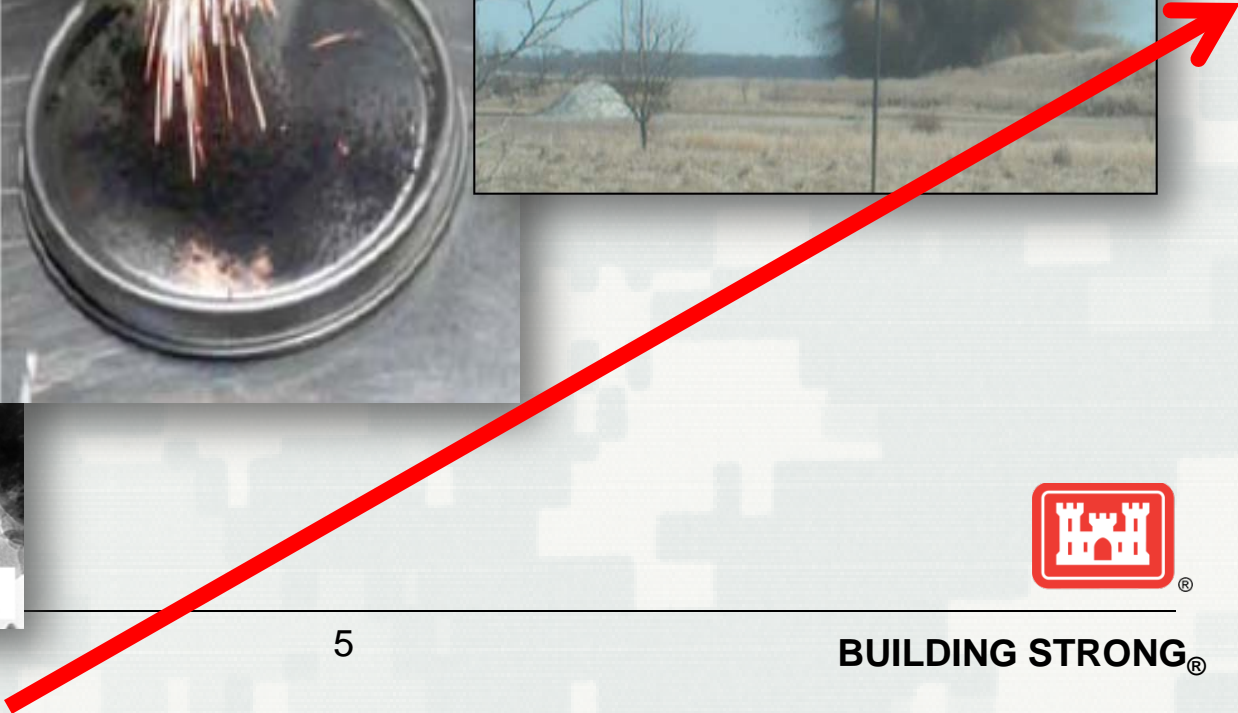
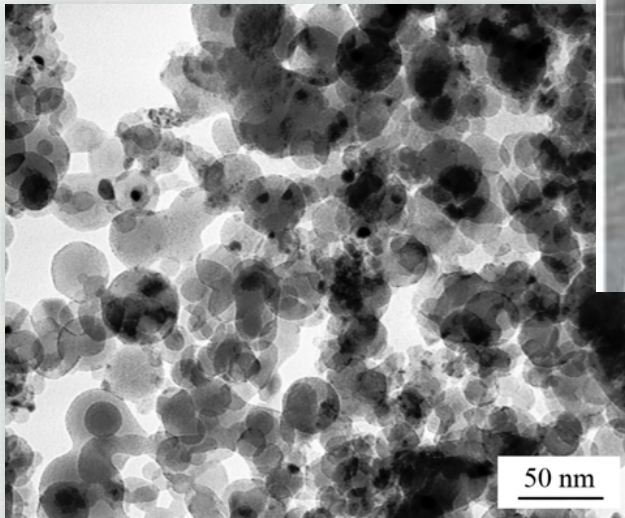
- (1) A multimedia environmental perspective built on a product life cycle framework is essential.
- (2) A by-product may be more problematic than the primary substance.
- (3) Human health is not the only issue of concern.
- (4) Use caution in generalizing from limited empirical data.
- (5) The public deserves to be well-informed.
- (6) Everything has trade-offs: some may be acceptable, some may not.
- (7) Even with limited information, technical experts may be able to anticipate risks.
- (8) An adaptive risk management strategy is critically important.



Adapted from Davis, 2007



ERDC CEA Case Study: Engineered Aluminum Nanoparticles



Applying CEA approach to nanotechnology in the R&D Phase

Known
Knowns

- Lack of mature industries
- Data lacking or evolving
- Characterization of materials
- Uncertainty is high
- Identify and prioritize knowledge gaps

Known
Unknowns

Unknown
Unknowns



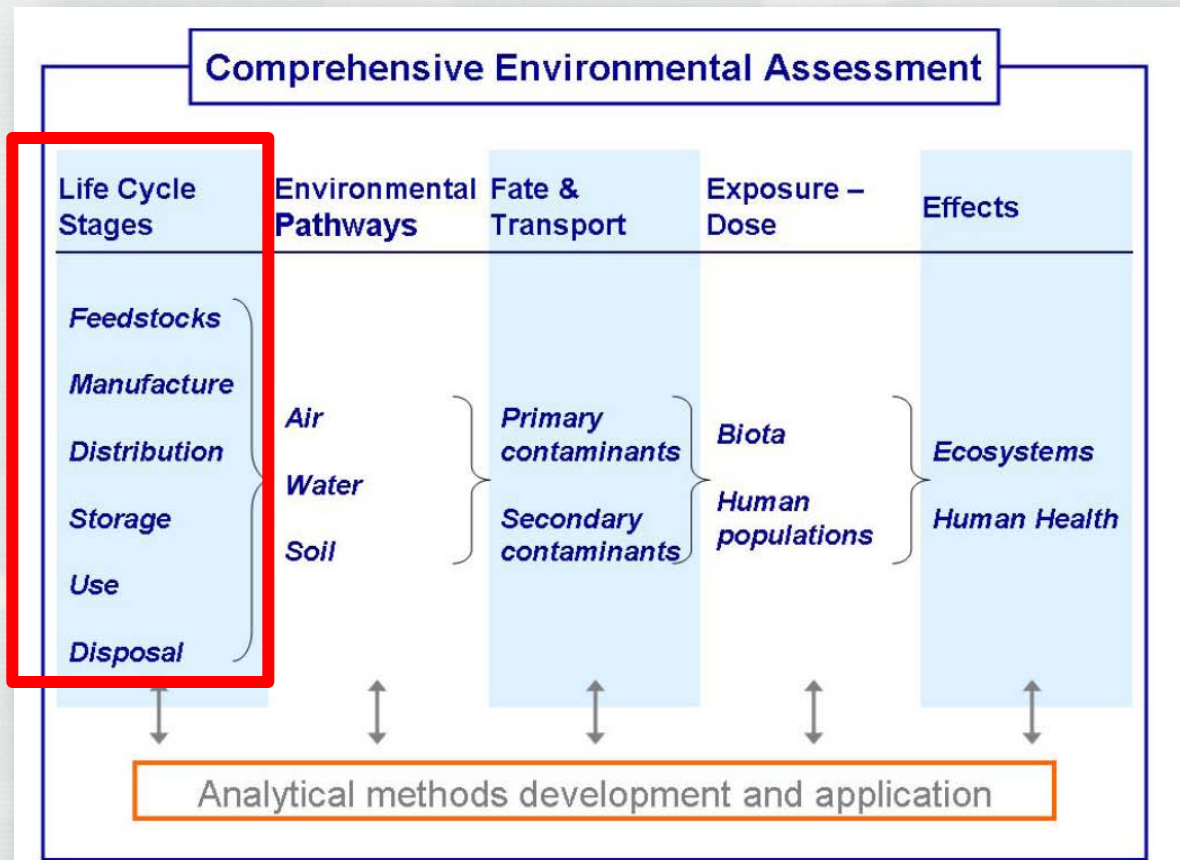
CEA Process

- **Identify the question(s)**
 - ▶ Sources
 - ▶ Life cycle stages, fate & transport, matrices, exposure, effects
 - ▶ Developed methods and standardized protocols
- **Obtain diverse perspectives**
 - ▶ **ODUSD** Chemical & Material Risk Management
 - ▶ **NNCO** National Nanotechnology Coordination Office
 - ▶ **ARMY-** ARDEC , Army Institute of Public Health, ERDC
 - ▶ **Navy-** NSWC-IHD
 - ▶ **Air Force-** Air Force Laboratory Human Effectiveness Directorate
- **Use collective judgment method**

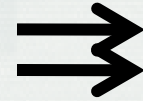
Adapted from Davis, 2007



CEA: Life Cycle Stages of nano-AI



Life Cycle Stages: Feedstocks & Manufacturing



Top-Down Synthesis

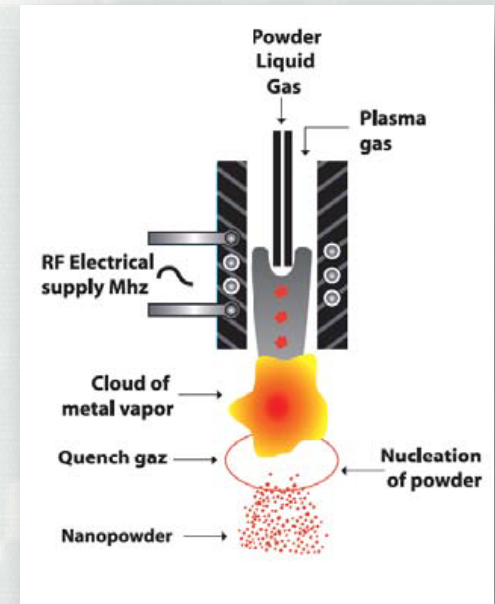
- Milling technique (micron-sized Al particles to nanosized powder)
- Vaporization technique (Al rods)

Bottom-up synthesis

- Solution technique

Both

- Plasma synthesis
- ARDEC Picatinney Arsenal Nanotechnology Research Center: Radiofrequency (RF) Induction Plasma reactor (Tekna Plasma Systems) pilot plant



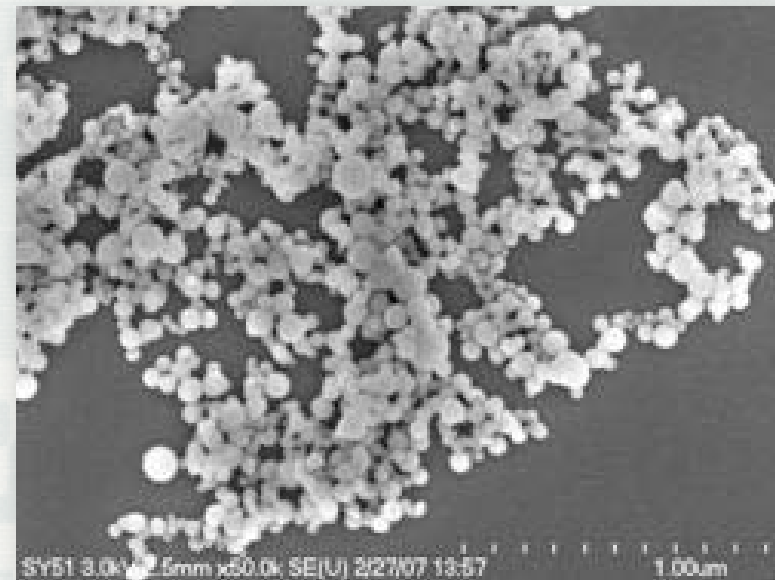
Synthesis Challenges: (1) Particle Sizes, (2) Nanoparticle oxidation



Life Cycle Stages – Distribution and Storage



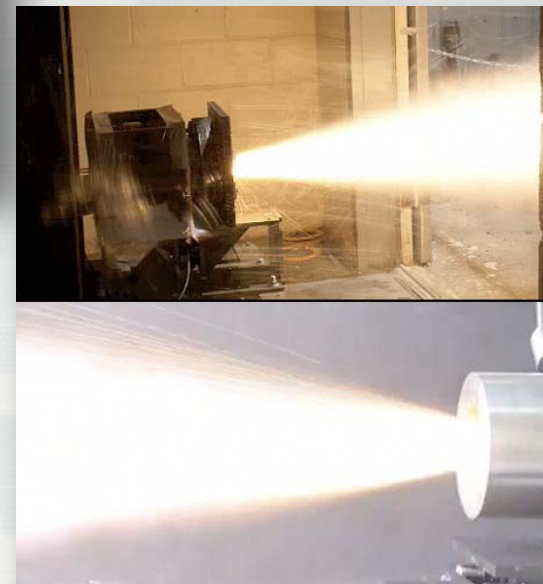
- Use of nano-aluminum still in the R&D phase
- Stored under inert atmosphere
- Aggregates are stored at the facility (still have research value),
- Current synthesis of 200g batches for rapid characterization
- Stability studies indicate no loss in surface area, however a 20% loss in reactivity due to oxygen diffusion



Life Cycle Stages – Use and Disposal

Potential Uses:

- Propellant
- Explosives
- Munitions primers
- Diesel fuel additive

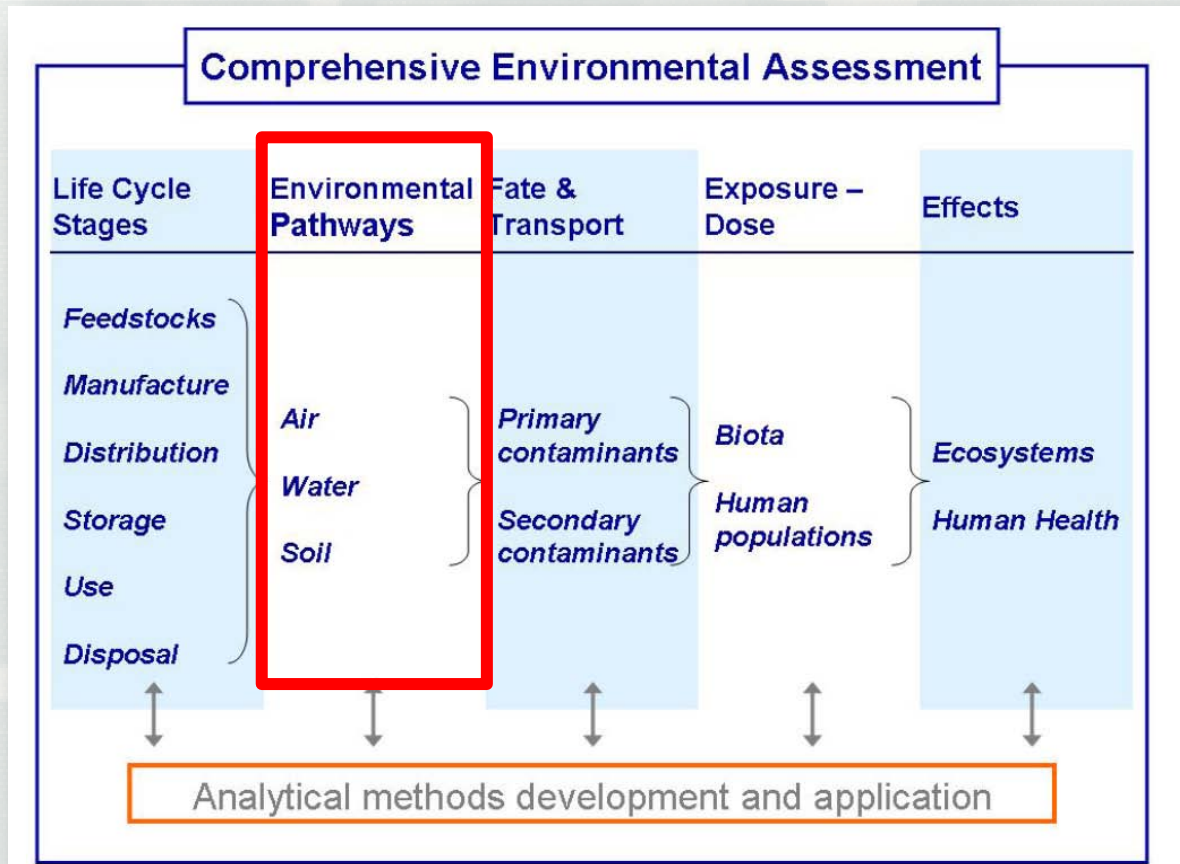


Potential Disposal Routes:

- Traditional landfills
- Wastewater streams
- Hazardous waste storage



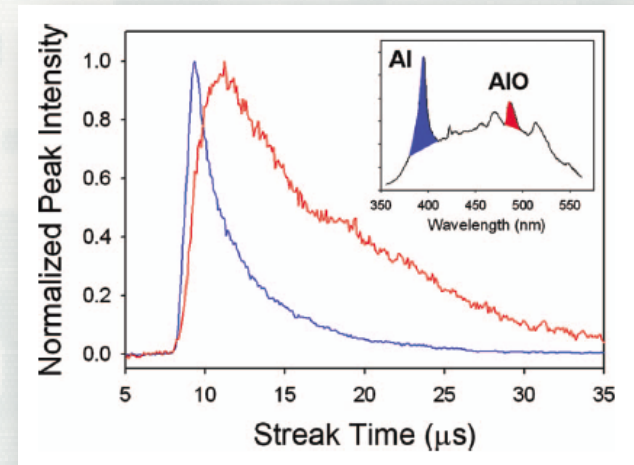
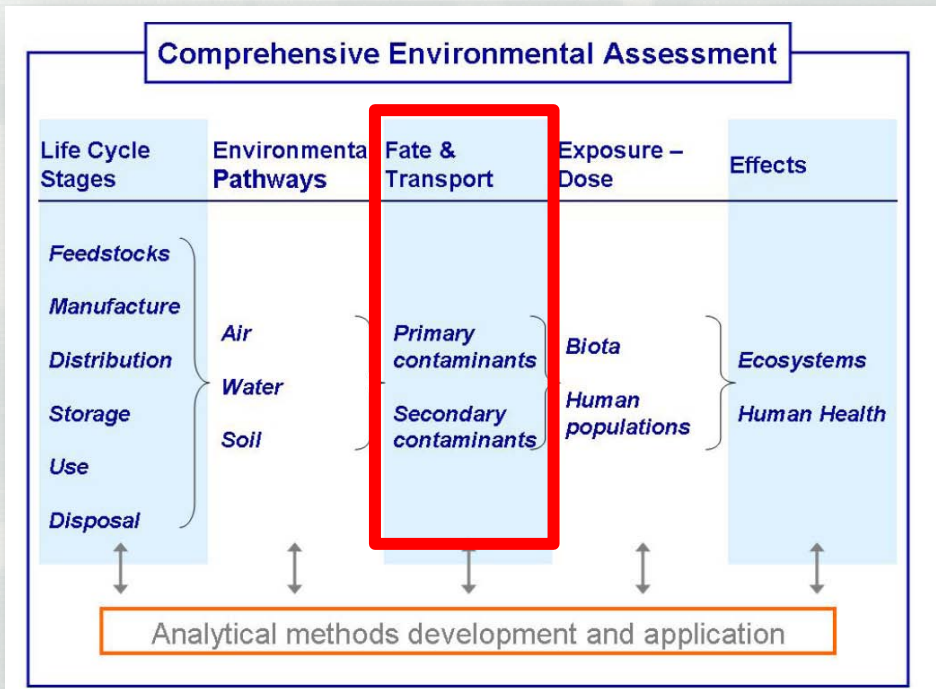
Environmental Pathways of nano-AI



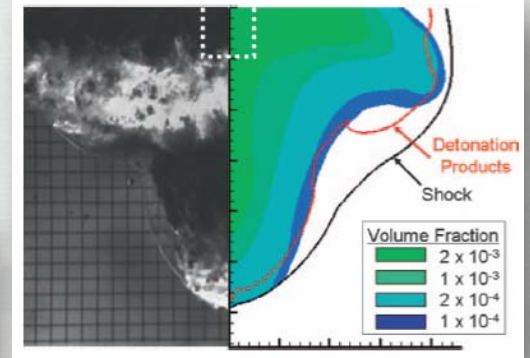
Most Likely Exposure Pathways:
Air > Soil > Water



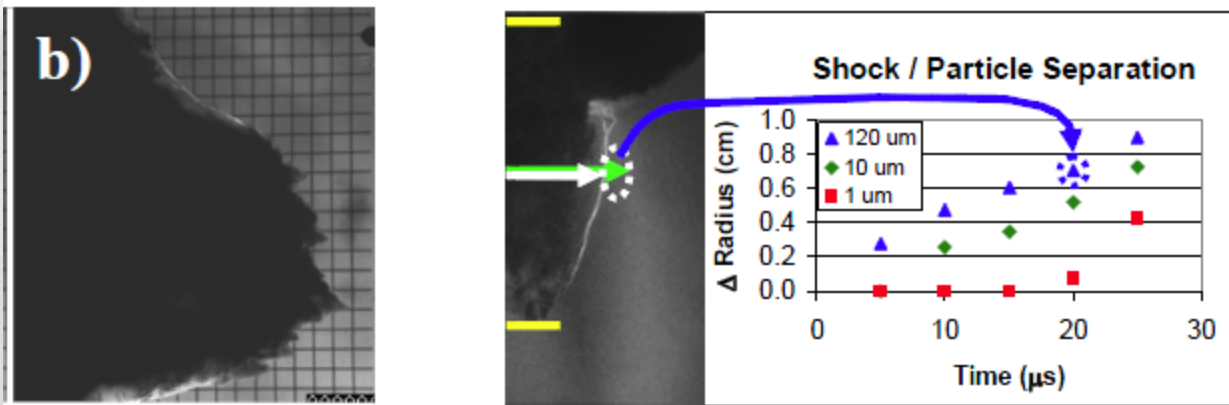
CEA: Fate and Transport of nano-Al



Carney et al. (2006)



Carney et al. (2009)

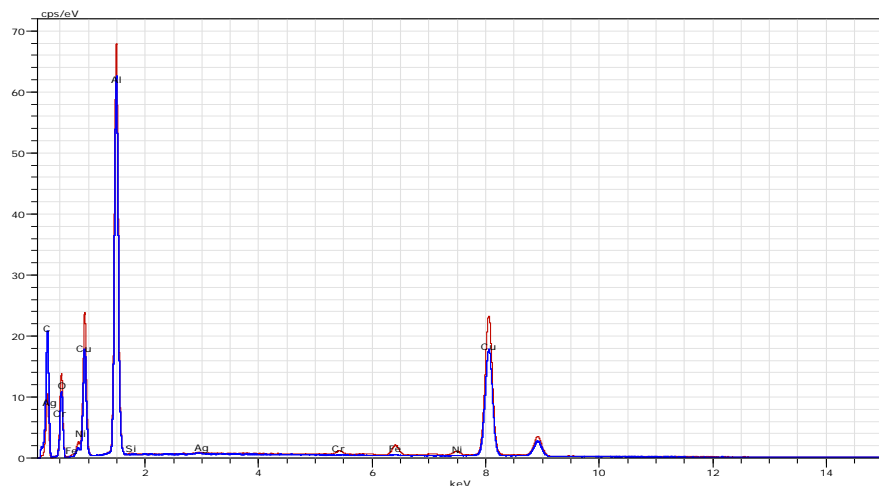
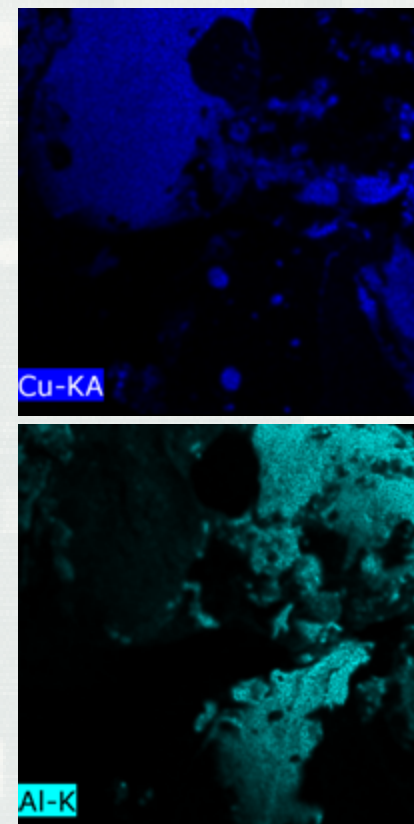
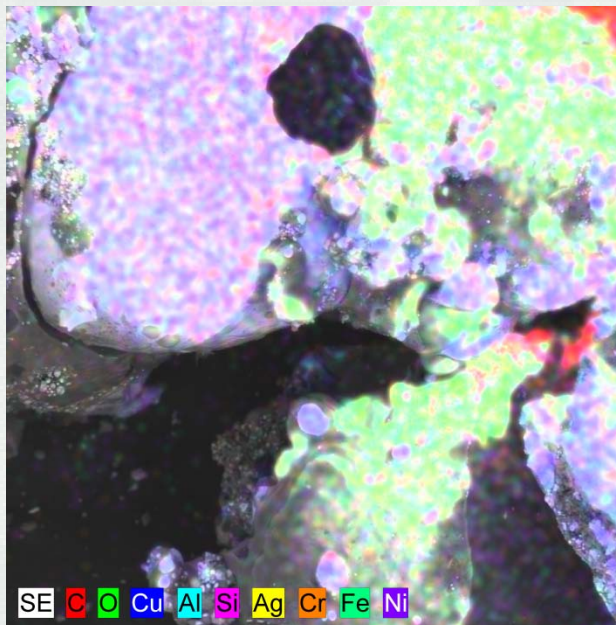
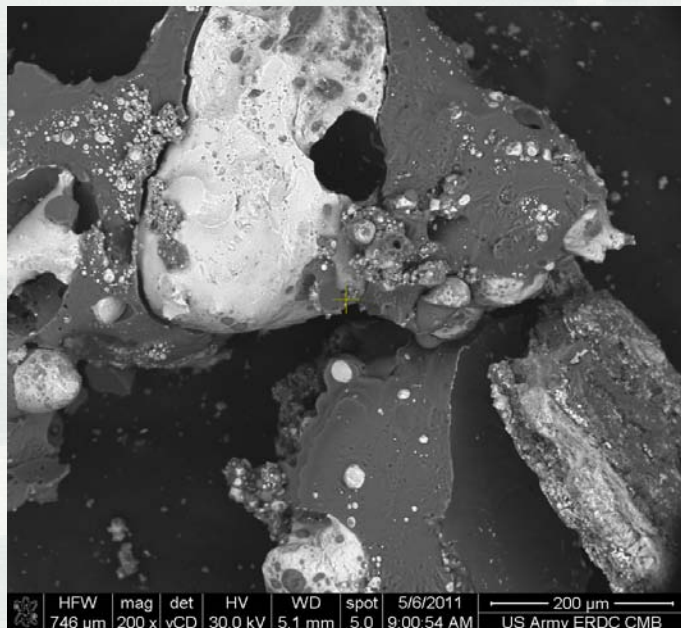


Carney et al. (2006)



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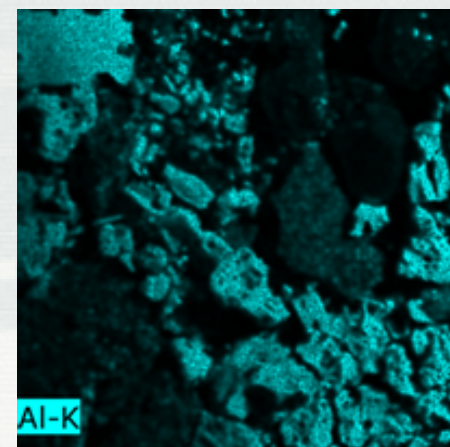
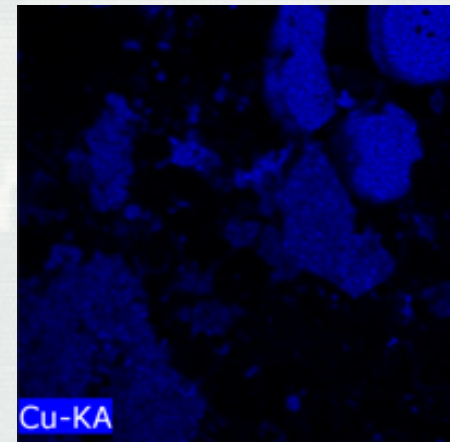
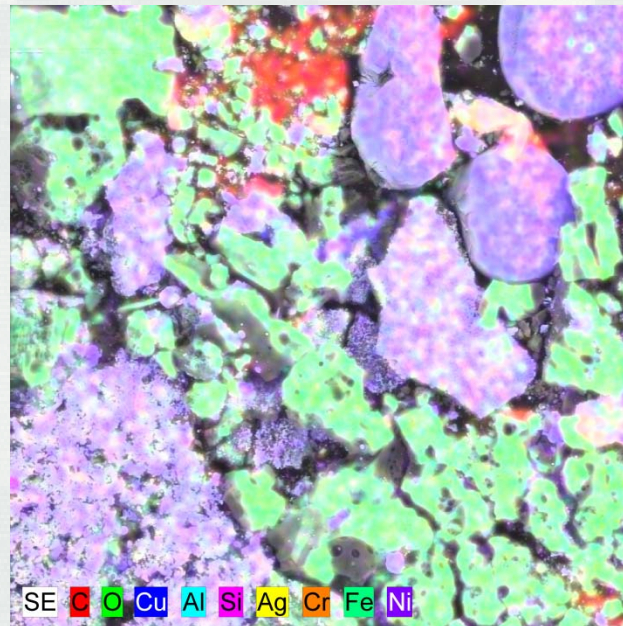
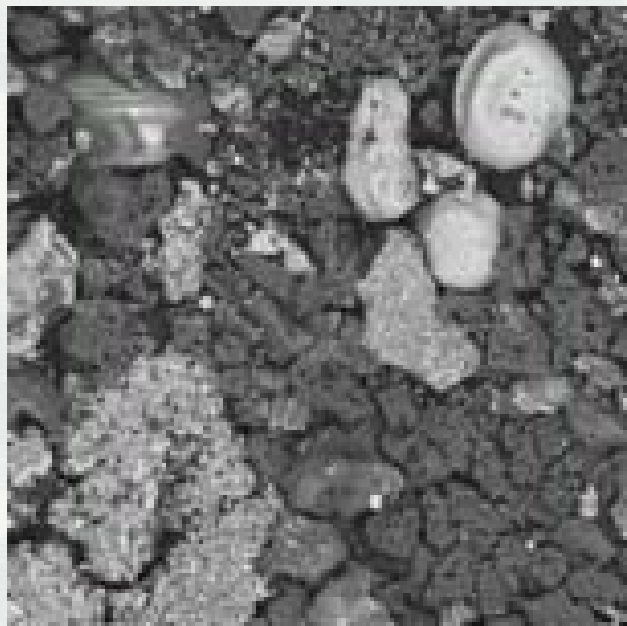
CEA: Simulated Explosion of CuO Nanorods and Al NPs



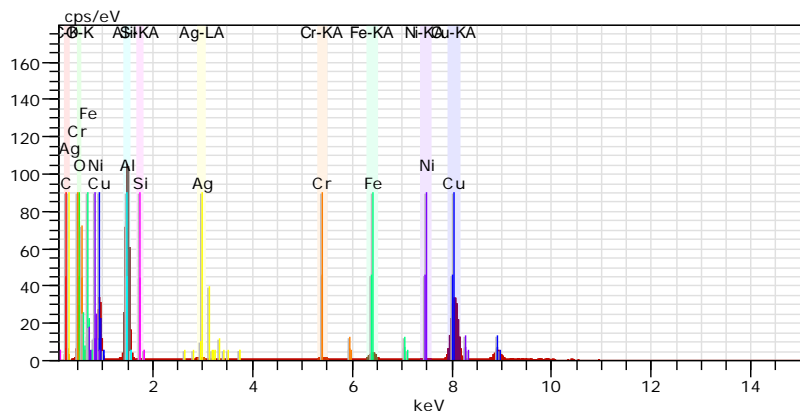
- Explosion resulted in sintered particles and nanosized metal particles
- Residue: 36.5% Al, 58% Cu





CEA: Simulated Explosion of CuO Nanorods and Al NPs



160,000x magnification

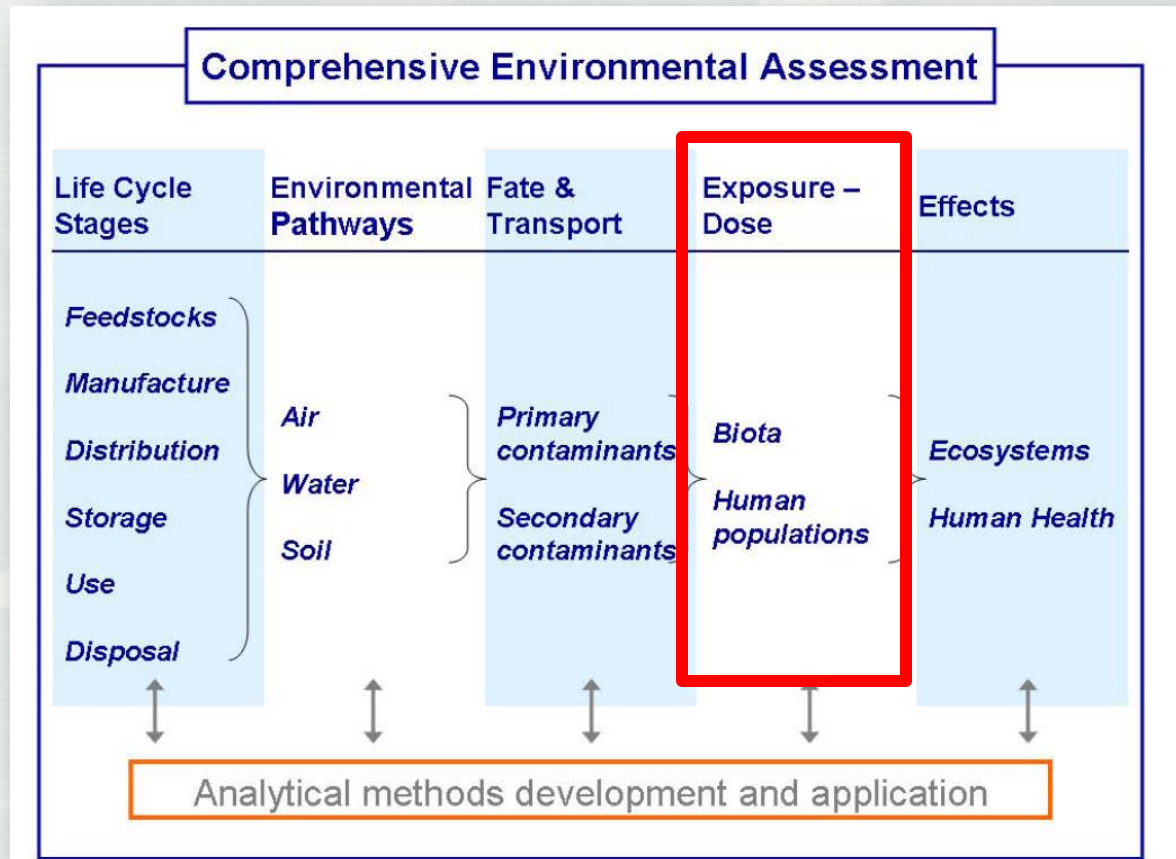


CEA: Fate and Transport of nano-Al

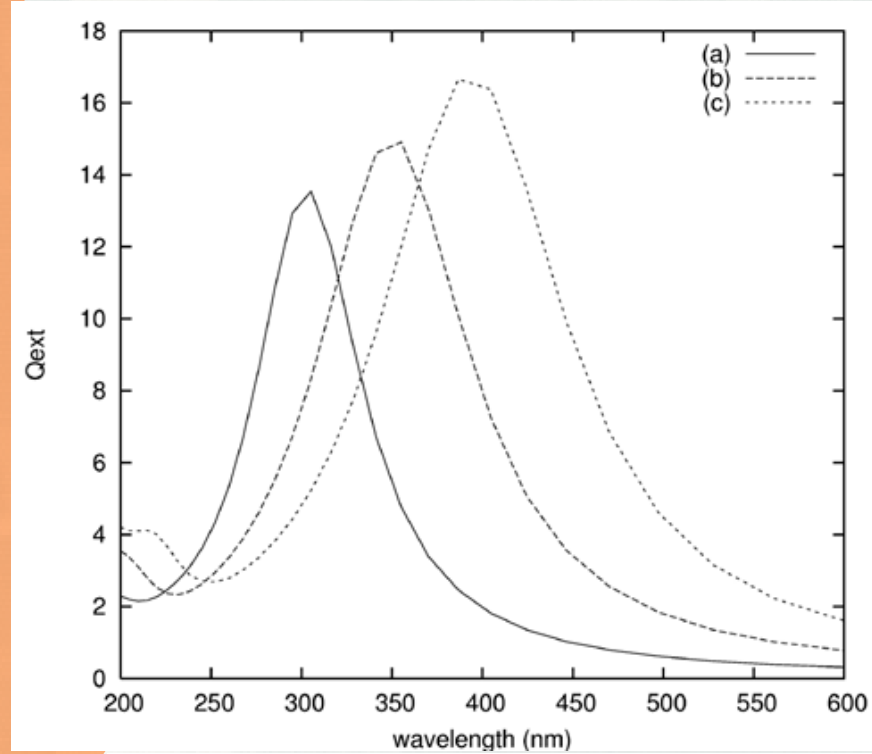
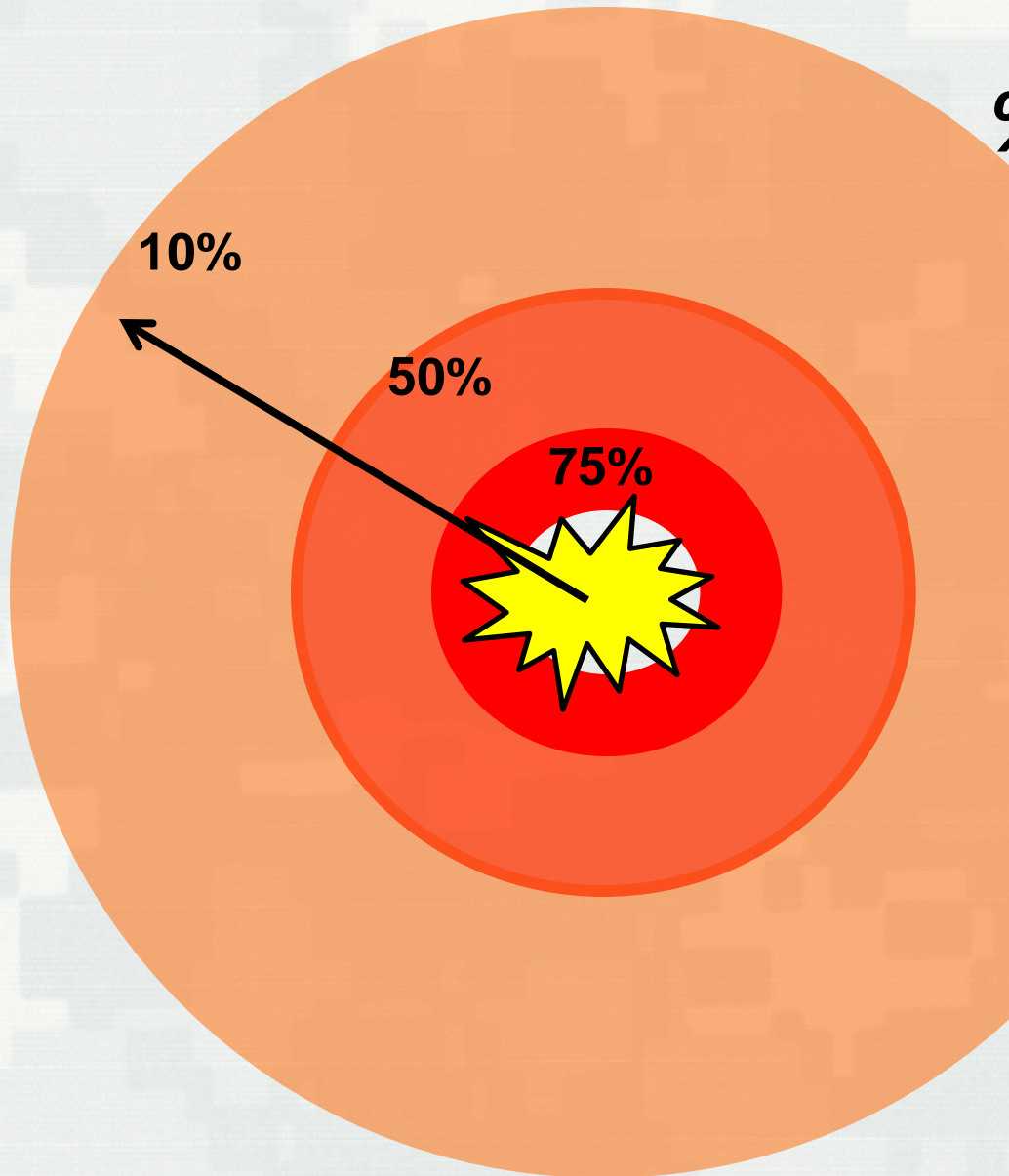
- Al is rapidly oxidized
 - Oxide coat stabilizes the particle and particle shape
- Particle size greatly influences oxidation potential
- Nano-Al/ Al_2O_3 interacts with soil ,water , and strongly with humic acids
- Highly agglomerates  affects mobility in soil
- Surface charge changes with leachate  alters mobility
- Micron-sized Al_2O_3 has greater sorption than nano- Al_2O_3



Exposure-Dose of nano-AI



Exposure-Dose % content of nano-Al



Plot of extinction values for Al triangular prisms (Faber et al. 2008)



Exposure-Dose of nano-Al

Most likely routes of nano-Al/ Al_2O_3 exposure:

Inhalation > Internal (mucociliary escalator) > Dermal > Internal (oral)



ARDEC-NIOSH collaborative framework “Nano-powder Synthesis & Associated Safety Precautions at ARDEC”

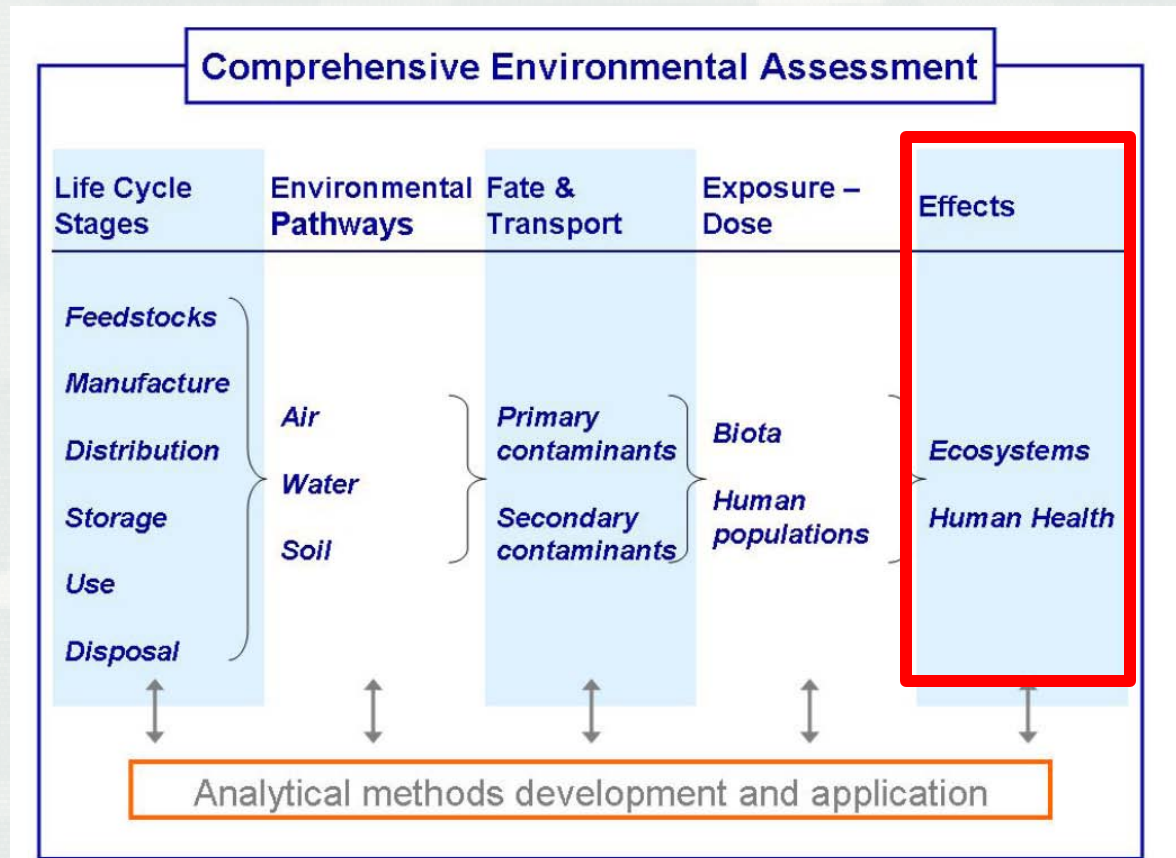
TWA and other occupational exposure values?

R&D laboratory evaluations of occupational exposures?

Evaluate exposures in the field and firing ranges

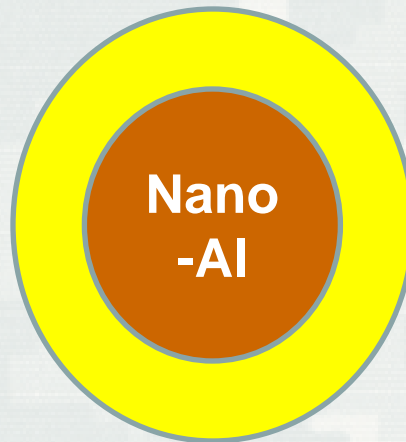


Effects of nano-AI

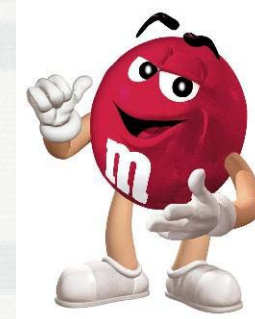
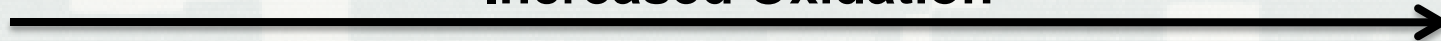


Problems with Effects of nano-Al

- Nano-Al/ Al_2O_3 is highly agglomerated
- Is aged nano-Al the same as nano- Al_2O_3 ?



Increased Oxidation



Effects of nano-Al: Ecosystems

Most Likely Exposure Pathways:

Air > Soil > Water

➤ Aquatic

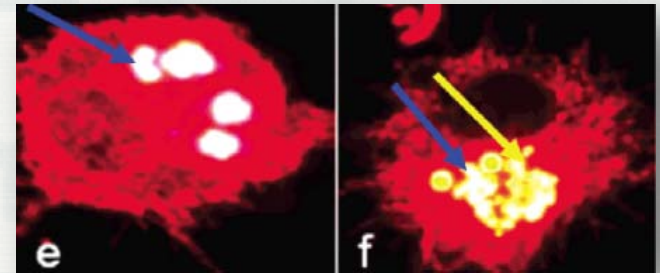
- **Less toxic to daphnids and algae than other NPs**
- **More toxic to juvenile zebrafish than adults**
- **Causes atherothrombotic events in zebrafish**
- **Produces differential effects on benthic organisms**

➤ Terrestrial

- **Mildly toxic to bacteria**
- **Mildly phytotoxic (root growth inhibition) due to ROS**
- **Soil nematodes and earthworm reproduction negatively affected, yet actively avoid nano-Al spiked soils**



Effects of nano-Al: Human Health



1. Inhalation

- Nano-Al, not Al_2O_3 , negatively affects alveolar macrophages function
- Suppressed macrophage ability to fight respiratory pathogen MRSA
- No *in vivo* studies yet

2. Dermal

- Dermal contact may increase proinflammation, dermatitis
- Accumulation likely in epidermis, but not dermis & no bioaccumulation

3. Internal

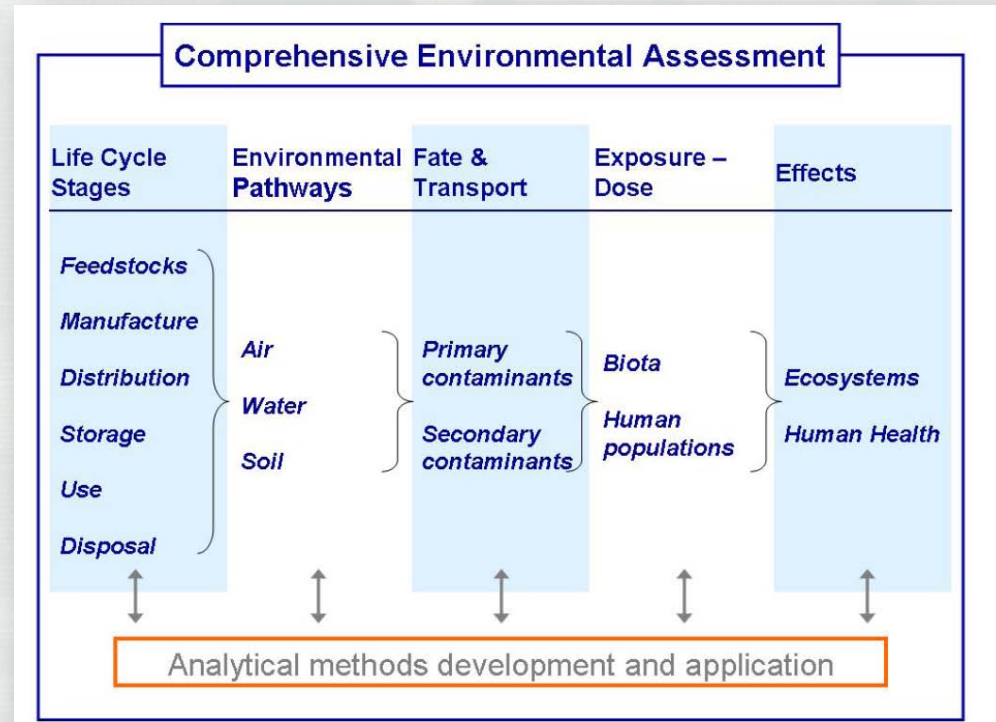
- Cell damage in several *in vitro* studies using internal organ cultures
- Neurotoxicity (blood brain barrier disruption) and



- Genotoxicity *in vivo* and *in vitro*, secondary to ROS (?)

CEA: Lessons Learned with fuel oxygenate MBTE

- (1) A multimedia environmental perspective built on a product life cycle framework is essential.
- (2) A by-product may be more problematic than the primary substance.
- (3) Human health is not the only issue of concern.
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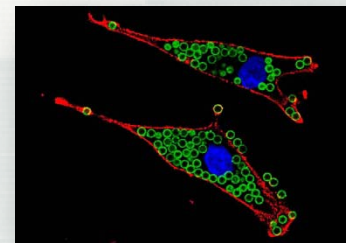
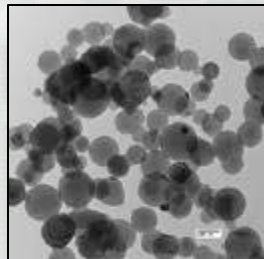


Adapted from Davis, 2007



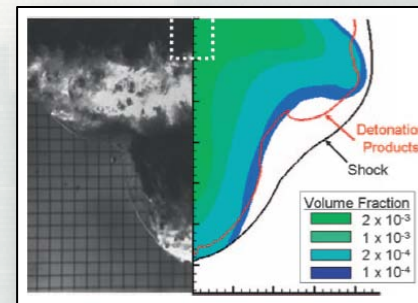
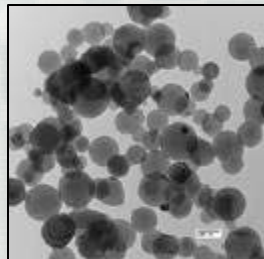
Preliminary Conclusions

- Potential sources and releases of nano-Al to the environment that will likely occur through air, water, or soil exposures through the production, use, and disposal of nano-Al propellants, igniters, and additives.
- However, these preliminary findings are the result of an assessment from the R&D community.
- Data collection is still required to gain a better understanding of the future deployment and handling of nano-Al as a military technology.



Data Gaps/ Moving Forward

- **Life Cycle:** Further collaboration required within the R&D community such as ARDEC, NSWC-IHD, and AFRL to discuss life cycle phases.
- **Environmental Pathways:** (1) combustion analyses, (2) atmospheric deposition field studies, (2) atmospheric modeling of firing ranges
- **Exposure:** *In vivo* exposure to biota and humans is perhaps the biggest area of uncertainty in this entire nano-Al CEA.
- **Environmental Fate:** (1) environmental characteristics (e.g., temperature, weather) effects on nano-Al aging, (2) field studies with military materiel (munitions, propellants, etc.)
- **Effects:** Data needs to reflect of actual particle sizes, i.e. nanoparticle agglomerates vs. monodispersed nanoparticles.





Risk Assessment Conceptual Model Builder [No Official Name]

Life Cycle Stages

Compartments



Wastewater



Air



Surface Water



Soil/Sediments



Landfills



Ground Water



Sediment

Organisms



Plants



Fungus



Animals



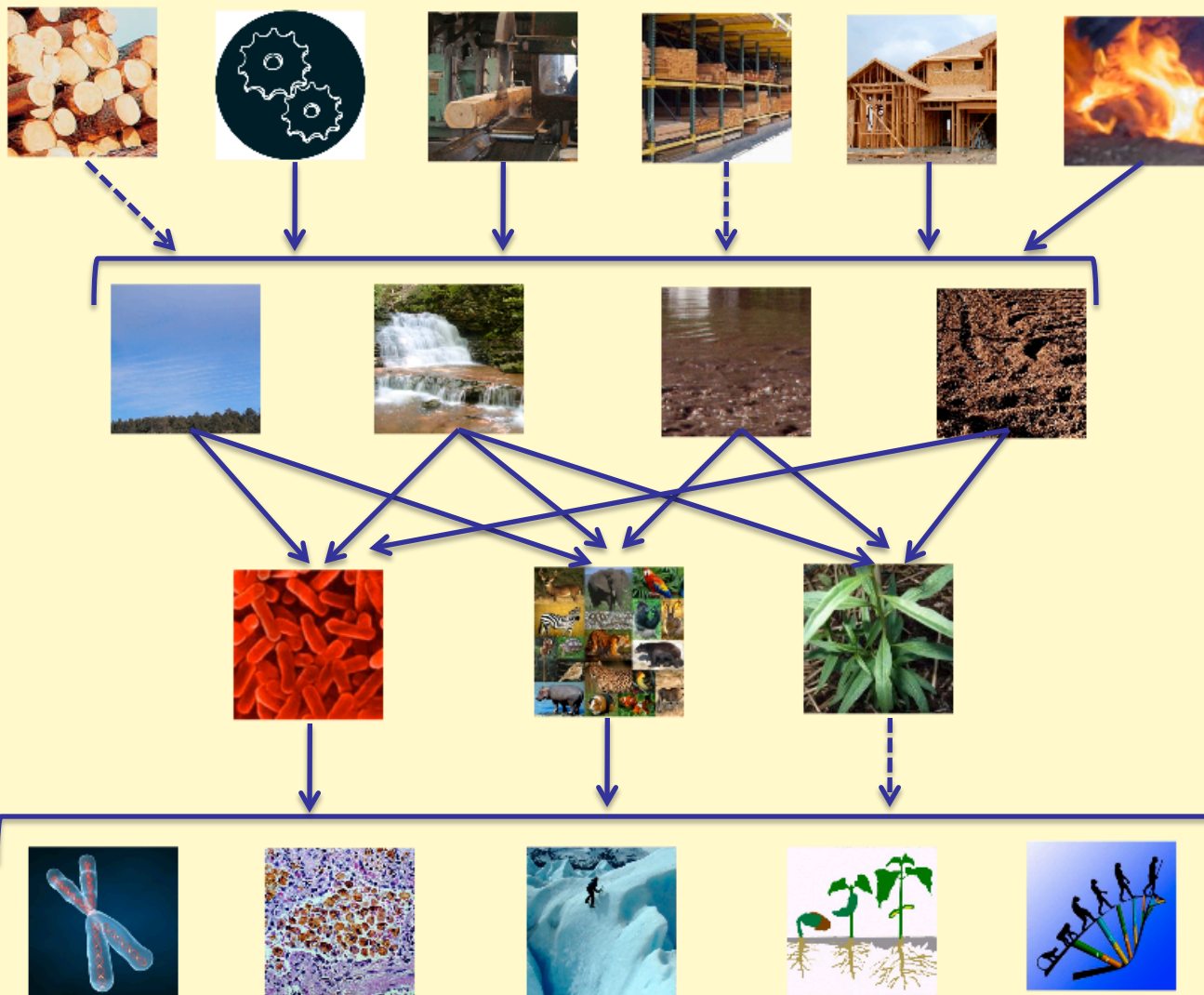
Humans



Bacteria

Ecosystems

Effects





Risk Assessment Conceptual Model Builder [No Official Name]

Life Cycle Stages

Compartments



Wastewater



Air



Surface Water



Soil/Sediments



Landfills



Ground Water



Sediment

Organisms



Plants



Fungus



Animals



Humans



Bacteria

Ecosystems

Effects



Raw Material

What is the name of the Material?

Is the process top down or bottom up (e.g., bulk material vs. seed process)?

What is the chemical composition and phase (e.g., solid, liquid, etc.) of the raw material(s)?

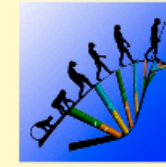
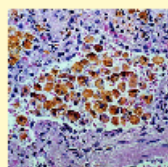
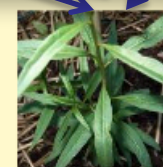
What other ingredients are used?

How much raw material and ingredients are needed per gram of final material produced (on mass basis)?

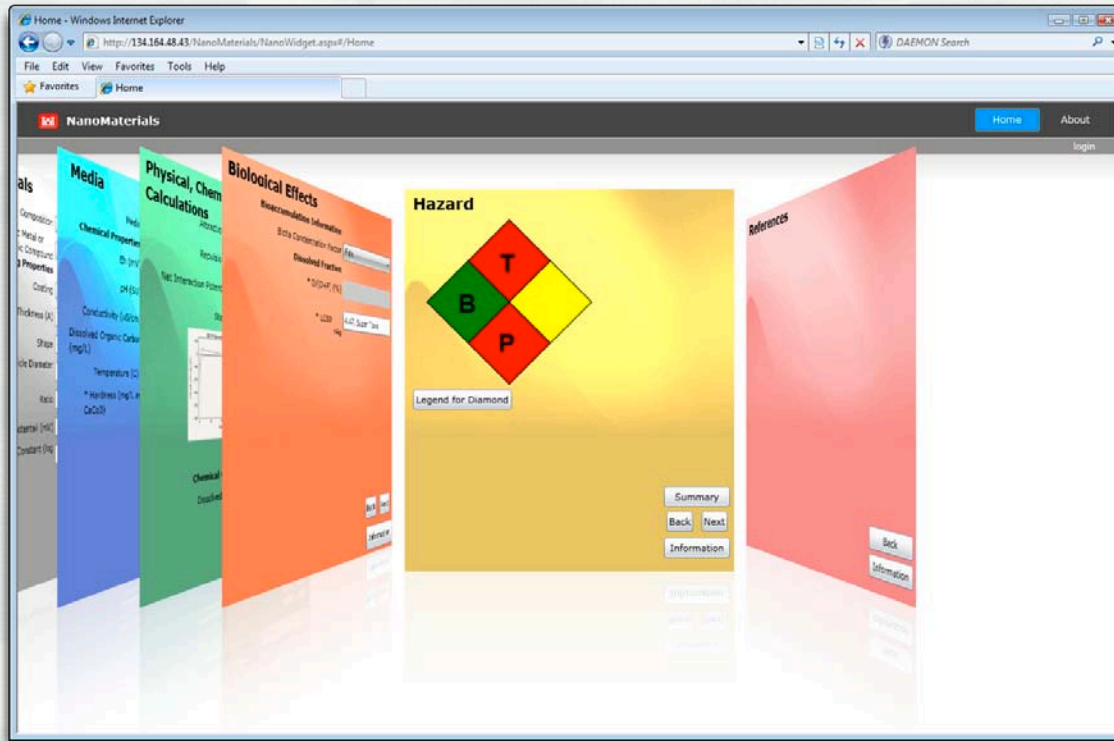
How much raw material, ingredients are used annually?

Cancel

Ok



NanoExPERT



Categories:

- Materials
- Media
- Physical, Chemical, Model, and Calculations
- Biological Effects
- Hazard



ERDC Environmental Nanotechnology Team

<http://el.erdcl.usace.army.mil/nano/index.html>

**Jeff Steevens-Senior Scientist,
technical lead**

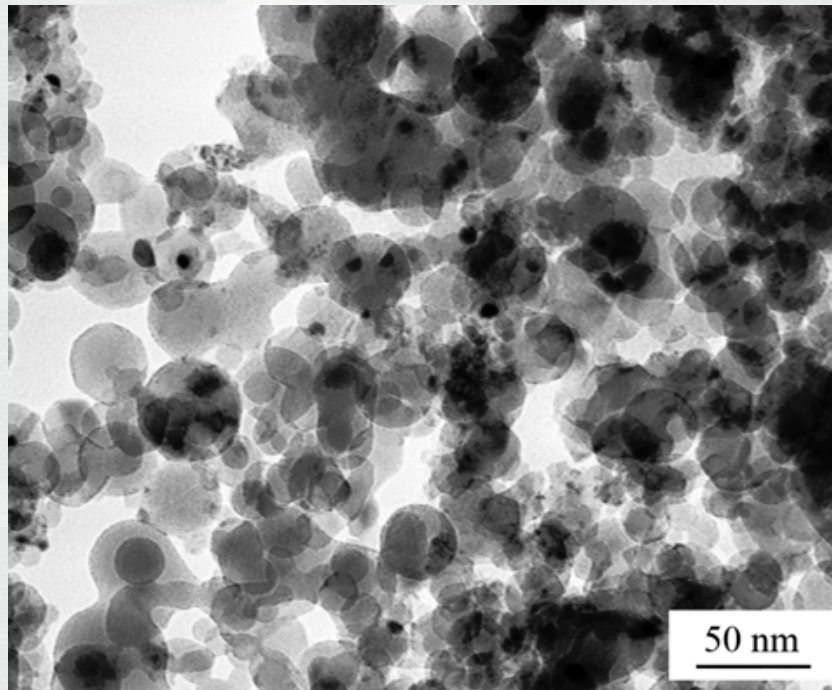
Chemistry: Anthony Bednar, Aimee Poda, Fran Hill, Rashid Mahbubur, Chris Griggs

Soil Science: Mark Chappell, Jen Seiter

Material Science: Chuck Weiss

Biology: Al Kennedy, David Johnson, Jacob Stanley, Cynthia Banks

Computer Science: Amy Bednar



- *Critical review and advising from Dr. Mike Davis, Senior Science Advisor, U.S. EPA and Dr. Thomas Seager, Professor, University of Arizona*
- *This research effort was funded by an ERDC Center Directed Research Project, “Comprehensive environmental assessment for nano-enabled defense and dual use capacities,” Dr. Jeff Holland, ERDC Director.*
- *Permission was granted by the Chief of Engineers to present this presentation.*
- *Opinions expressed during this presentation are those of the author and not of the USACE or Army.*

