Environmental Consequences of Nanotechnologies

Engineer Research and Development Center

Jeffery A Steevens, Senior Scientist
Alan Kennedy, Jessica Coleman, Zach Collier, Robert Moser, Aimee Poda, Charles Weiss
US Army ERDC

Mark Widder and MAJ Jonathan Stallings
US Army Center for Environmental Health Research

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Nanotechnology Working Group
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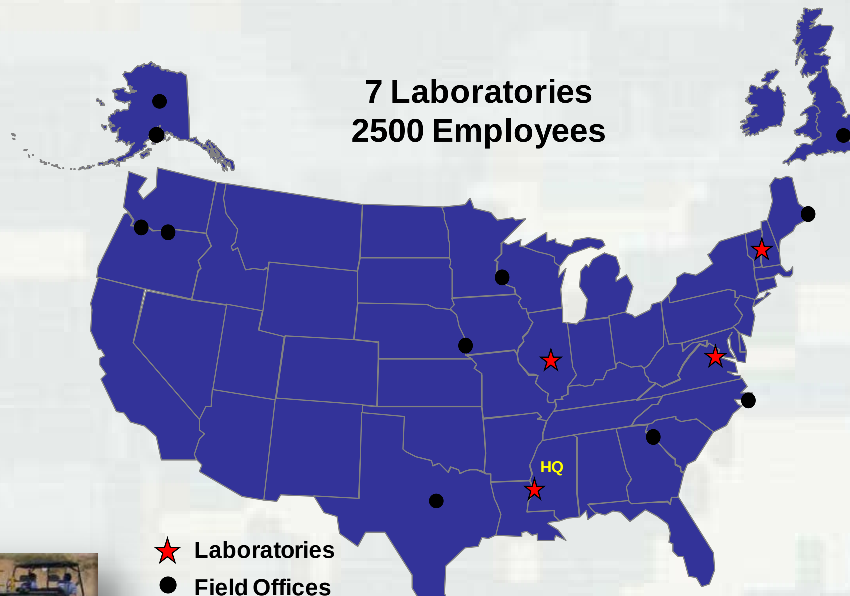
US Army Corps of Engineers®

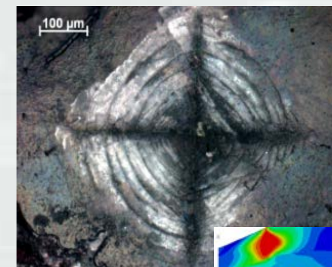
ERDC
Engineer Research and Development Center

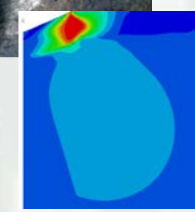
US Army Engineer Research and Development Center

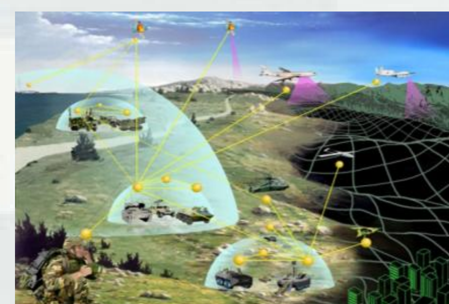
Research Areas

- Civil Works/Water Resources
- Environmental Quality/Installations
- Military Engineering
- Geospatial Research and Engineering



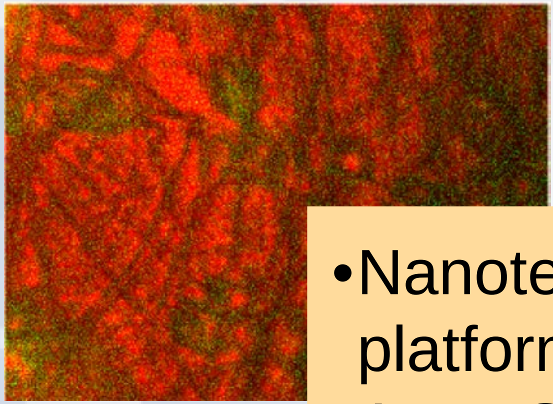




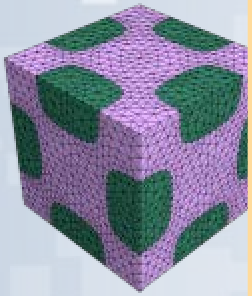
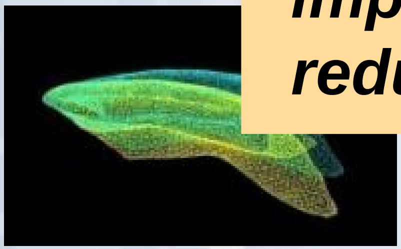
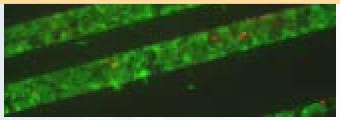


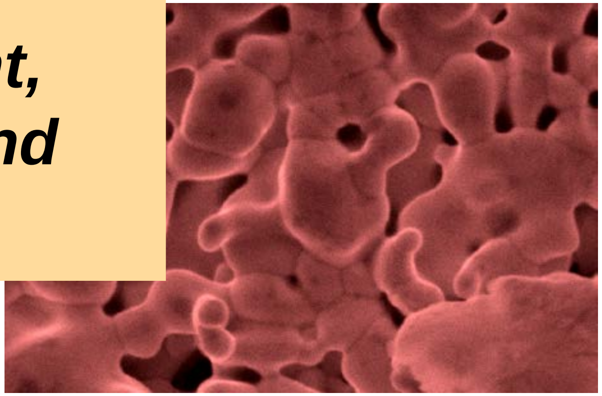
Innovative Solutions for a Safer, Better World

Why Army?

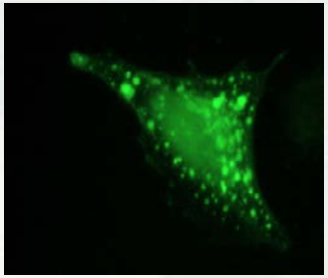


- Nanotechnology will impact *ALL* Army platforms.
- Army S&T investment will enable dramatic improvements in: ***force protection, ease overburdened Soldiers, reduce logistics burden, create operational overmatch, operate in CBRNE environment, improve operational energy, and reduce life-cycle costs***

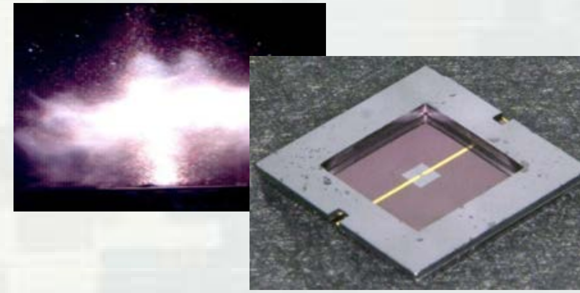


Army Technologies using Advanced Materials



NP for targeted anti-cancer

Composite food pouches

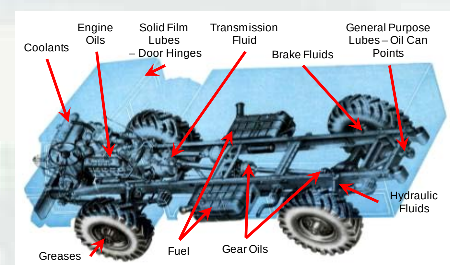


Explosives

Carbon nanotube pyrophoric

Body Armor

Transparent Armor



Lubricants and fluids

Environmental Life Cycle of Advanced Materials and Chemicals

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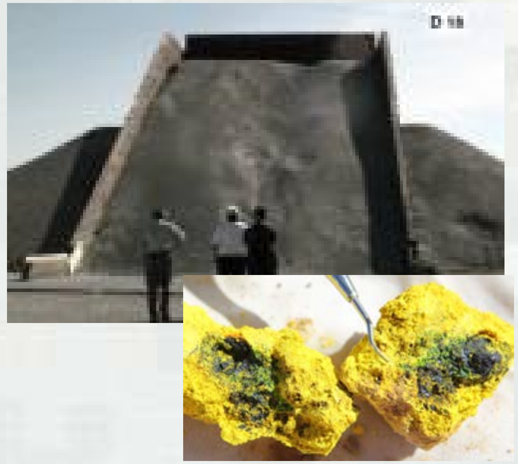
Carbon Nanotube Pyrophoric



Depleted Uranium

IMX 101

Goal: Proactively support Army technology research and development

1) Determine <u>critical risk parameters</u> such as fate, transport, and toxicity
2) Develop mechanistic and molecular models for <u>predicting risks</u>
3) Use <u>life cycle approach</u> to enable acquisition process for delivering safe technologies to the soldier

Life Cycle of Technology

Technology Life Cycle

Raw Materials → Production → Manufacture → Deployment and Operations → Disposal / Recycling

Releases to Environment

Conceptual Model, Characterization, Risk Analysis

Emerging Defense Technologies

- Coatings
- Energetics
- Penetrators
- Textiles
- Composites

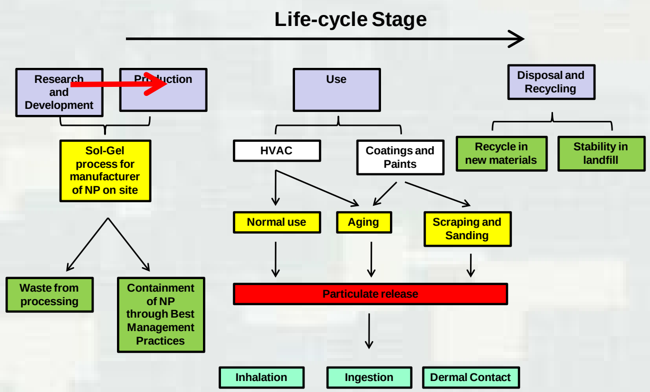
Acquisition Support

- Research and Development
- Management
- Regulatory Compliance
- Decision Analysis

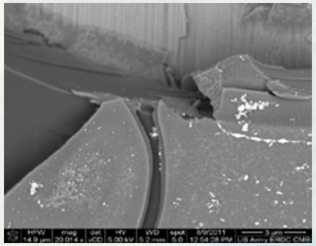
Release and Toxicity of NP from Self-Decontaminating Surfaces

DTRA
Defense Threat Reduction Agency

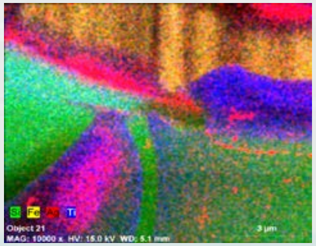
- Comprehensive environmental assessment used to identify data gaps
- Address uncertainties to support technology development
  - Release from substrate, particle characteristics
  - Toxicity screening using mixed alveolar cell culture



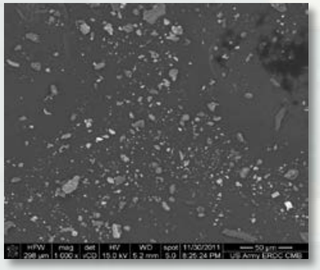
Conceptual model to identify data gaps, releases, and routes of exposure

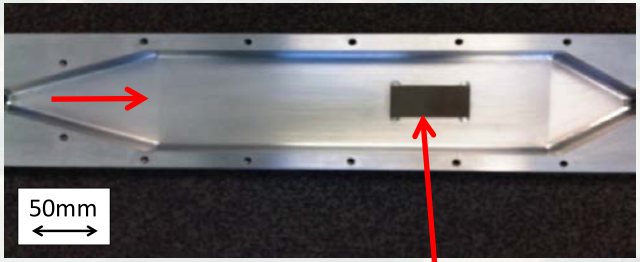


(a) Backscattered SEM micrograph of SDS

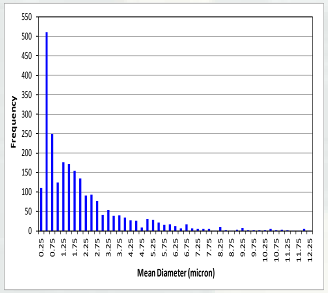


(b) EDS mapping of Si, Fe, Ag, and Ti





Coupon



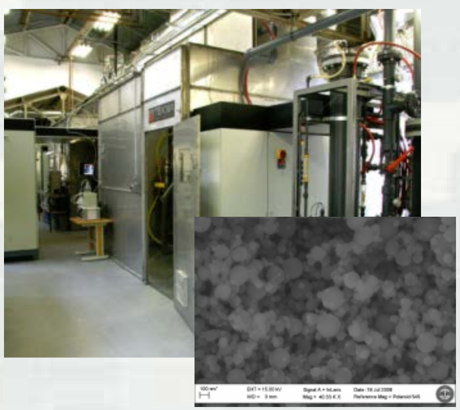
Adhesion and air flow release testing of coating coupon. SEM/particle size analysis of particles released from surface, Steevens et al., 2012

Results supported development of SDS technology

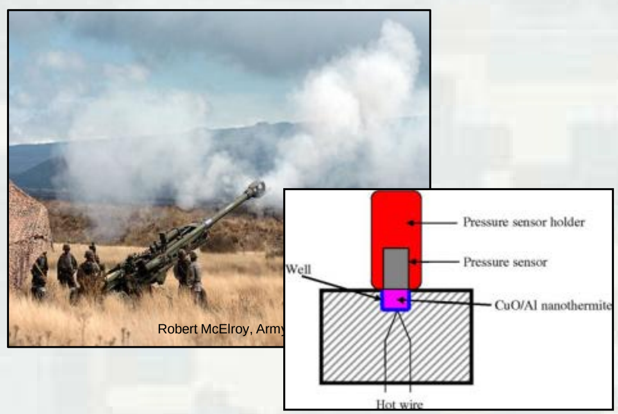
Environmental Life Cycle of Nanothermites

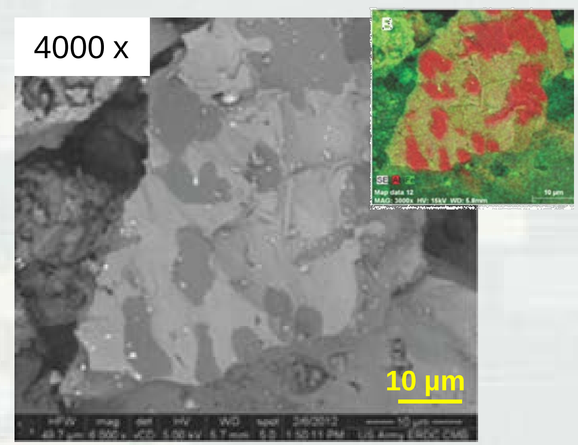
- **Aluminum + reducing agent (Fe_2O_3 , Bi_2O_3, or CuO)**
- **Releases and risks evaluated over life-cycle**
- **Focus on release during use: transformation, fate, exposure, toxicity**
- **Enables informed decisions regarding safety <u>and</u> informs/proactively addresses regulations**

Research / Production → **Use**



Tekna plasma system for nanoscale Al (above); SEM of nanoscale aluminum (below), Chris Haines, ARDEC

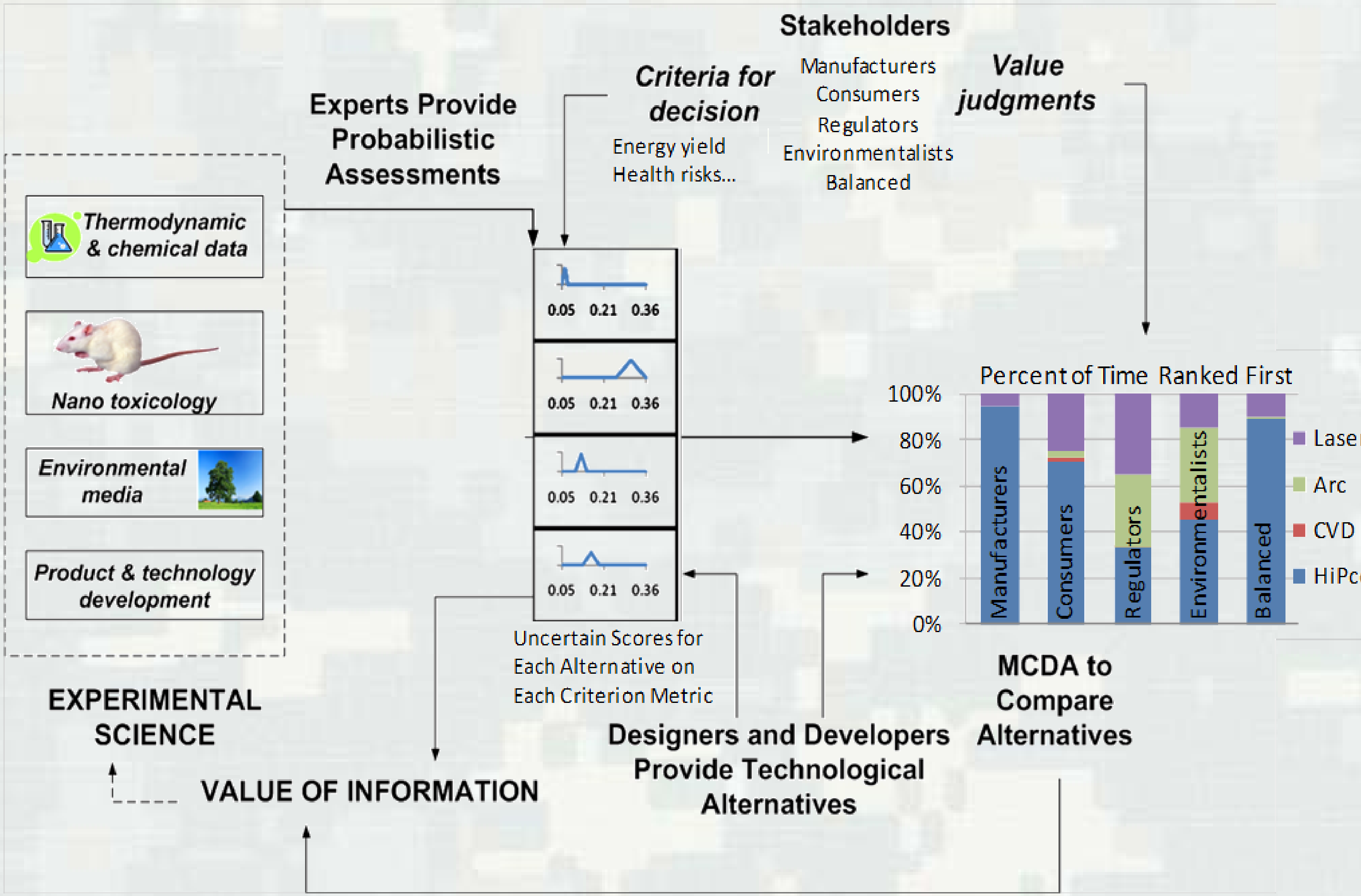




Scanning electron microscope image of Al/Fe_2O_3 energetic residue showing wide range of particle size; many greater than 1 µm

Results guided Army decisions on development of nanothermites

Framework for Integrating Physical & Social Science



How do we make decisions when there is not enough data or there is uncertainty in the data?

Linkov et al., Nature Nanotechnology 6,784–787(2011)

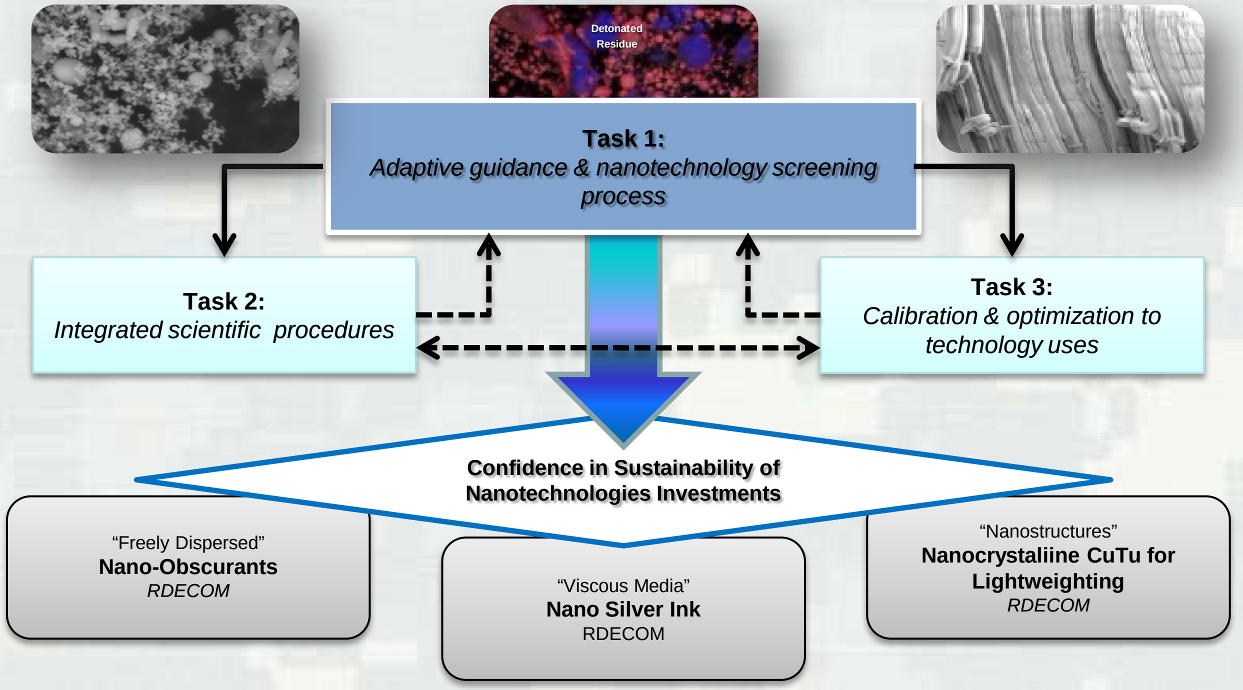
nature nanotechnology LETTERS
PUBLISHED ONLINE: 2 OCTOBER 2011 | DOI: 10.1038/NNANO.2011.163

Environmental Consequences of Nanotechnologies

Program FY14-18

Address stated Army PEO/PM/user priorities and needs:

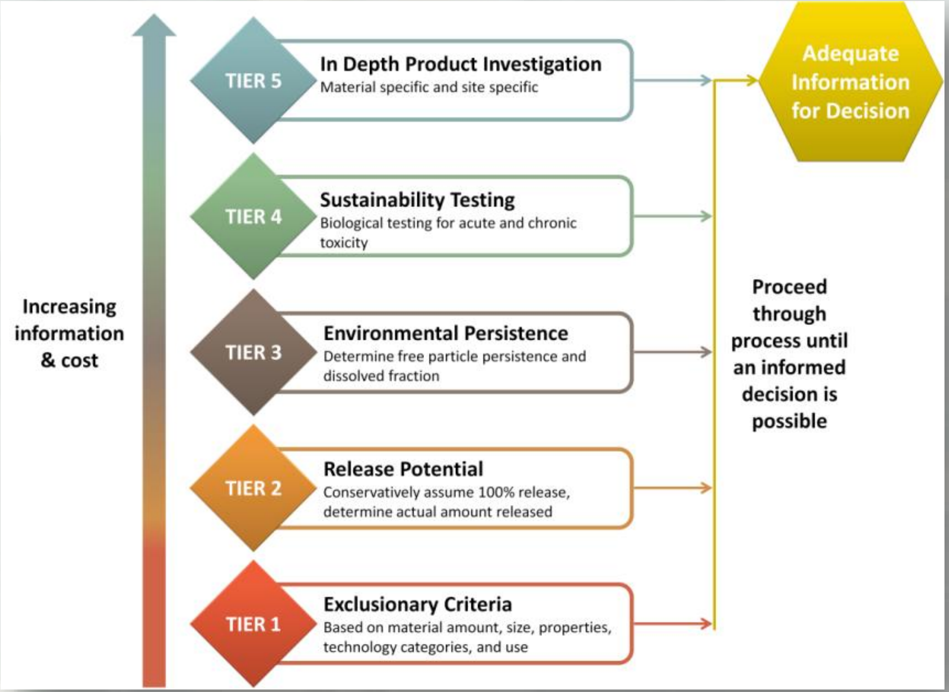
1. Establish consistent EHS methods to assess Army nanotechnologies and meet acquisition goals
2. Define risk management for diverse applications (nano-particle, nano-feature, nano-product)
3. Consider relevant use of technologies & develop the industry standard

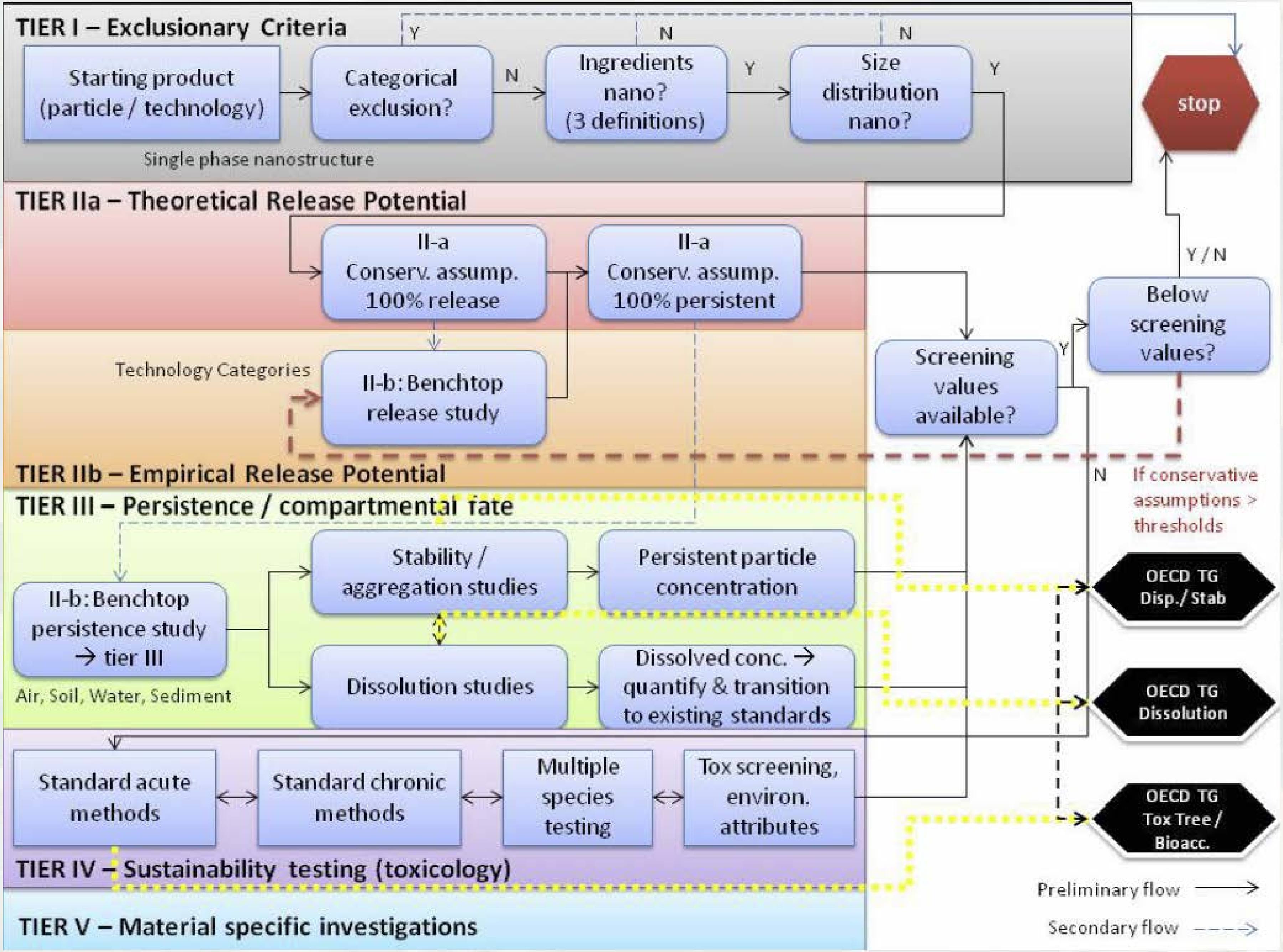


Task 1: Framework
Environmental Risk Decision Criteria for Nanomaterials

Framework

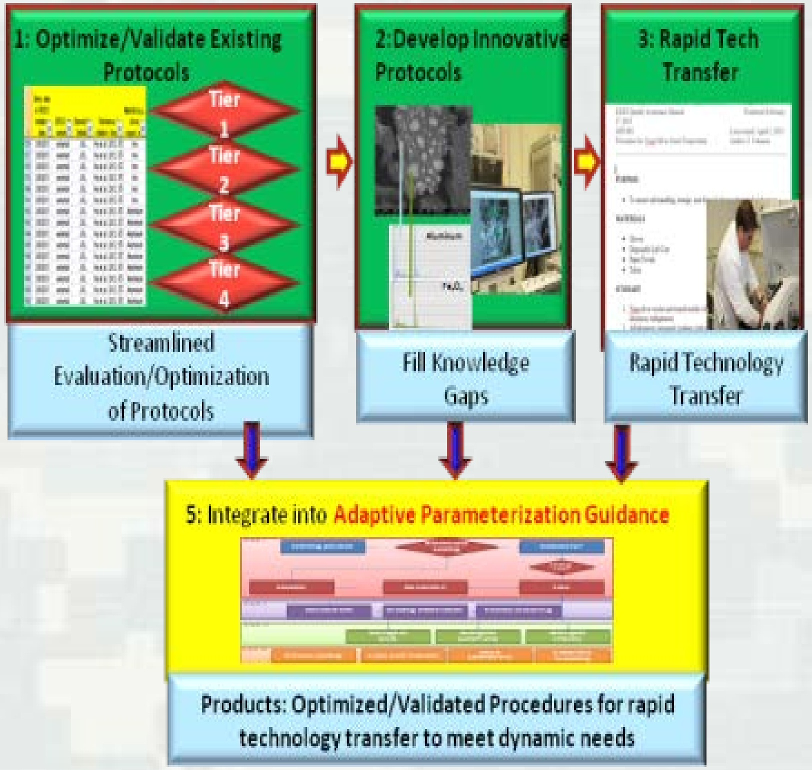
- Develop tiered process for providing all needed EHS data
- Tiered process (termination points)
- User-friendly web tool: guides the EHS compliance process
- Tie to regulatory community




TIER I – Exclusionary Criteria
Starting product (particle / technology)
Categorical exclusion?
Ingredients nano? (3 definitions)
Size distribution nano?
Single phase nanostructure
Y
N
N
N
Y
Y
stop
TIER IIa – Theoretical Release Potential
II-a Conserv. assump. 100% release
II-a Conserv. assump. 100% persistent
Technology Categories
II-b: Benchtop release study
Screening values available?
Y
Below screening values?
Y / N
N
If conservative assumptions > thresholds
TIER IIb – Empirical Release Potential
TIER III – Persistence / compartmental fate
II-b: Benchtop persistence study → tier III
Air, Soil, Water, Sediment
Stability / aggregation studies
Persistent particle concentration
Dissolution studies
Dissolved conc. → quantify & transition to existing standards
OECD TG Disp./Stab
OECD TG Dissolution
OECD TG Tox Tree / Bioacc.
Standard acute methods
Standard chronic methods
Multiple species testing
Tox screening, environ. attributes
TIER IV – Sustainability testing (toxicology)
TIER V – Material specific investigations
Preliminary flow
Secondary flow

Task 2: Standard Operating Procedures

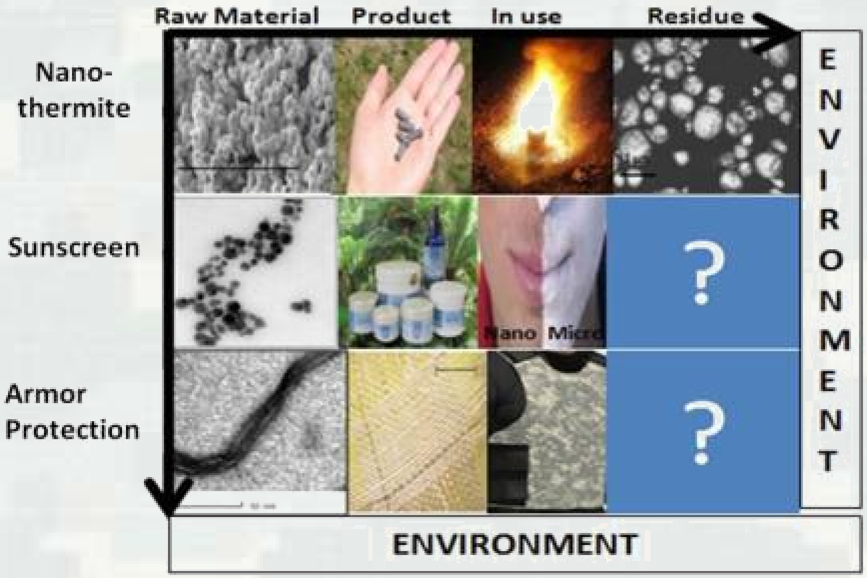
- **Central repository**
  - Connection to framework
  - Acquire existing SOPs for reference (e.g., NIST, CEINT, NCL, OECD, ISO)
  - Reference standard based
  - Scientific procedures to fill data gaps
    1. Particles
    2. Technologies
  - **Product**: On-line technical SOPs relevant to Army applications



Task 3: Technology Case Studies

Test, characterize and optimize the EHS framework

- For relevant Army technologies
- Regulatory paradigm shift from ingredients to in use release
- Compare EHS of free particles vs. in-use technology
- Acquire 3~5 technologies



Technology categories:

1. **Freely dispersed** (e.g., obscurant)
2. **Viscous media** (e.g., sunscreen)
3. **Diffuse coatings** (e.g., textiles)
4. **Composites** (e.g., EMI, armor)
5. **Nanostructured materials** (e.g., threat detection, remediation)

Task 4: Standardization for Army Technology Progression

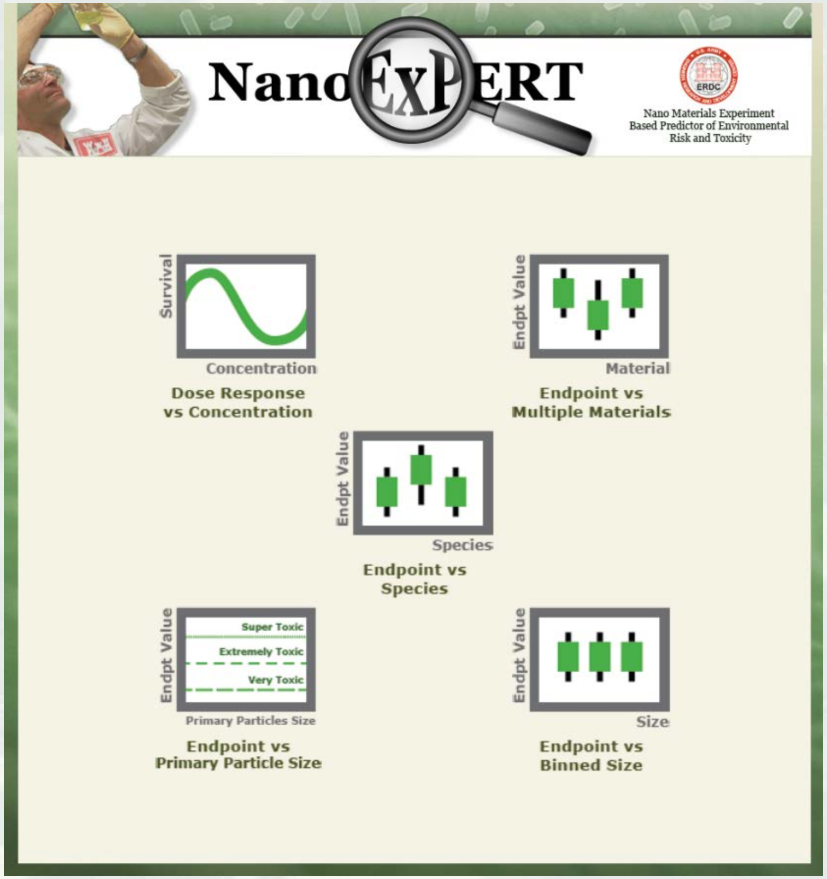
- **Internal coordination**
- **External collaboration**
  - EPA, ILSI Nanorelease
- **Test method development**
  - ERDC Technical Notes
  - OECD
    - ERDC leading 2 TGs (dissolution, aquatic tox)
    - ERDC participating in 3 addition TGs (bioaccumulation, dispersion/stability, categorization)
    - Looking for collaborators!
  - ASTM: E56
    1. Framework
    2. Scientific method

Tools and Databases

NanoExPERT

10 TOOLS

- Synthesis tools
  - Toxicity thresholds
  - Bioaccumulation
  - Environmental modifying factors
  - Dose metric conversion
- Calculators
  - Surface area
  - Number density
  - DLVO
- Conceptual
  - CEA conceptual model
  - Soil map

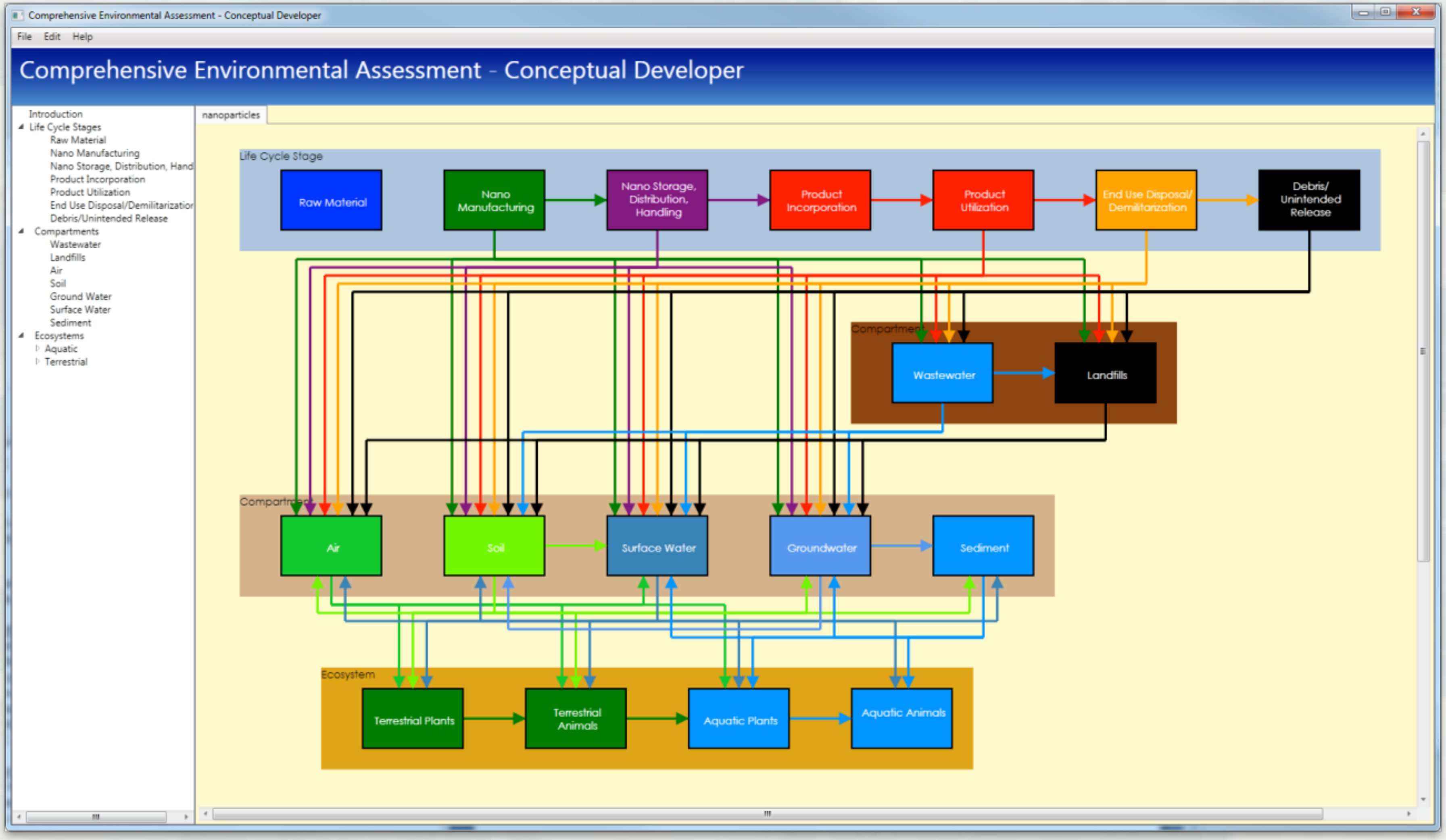


https://nanoexpert.usace.army.mil/

http://youtu.be/ficQV5XriC8

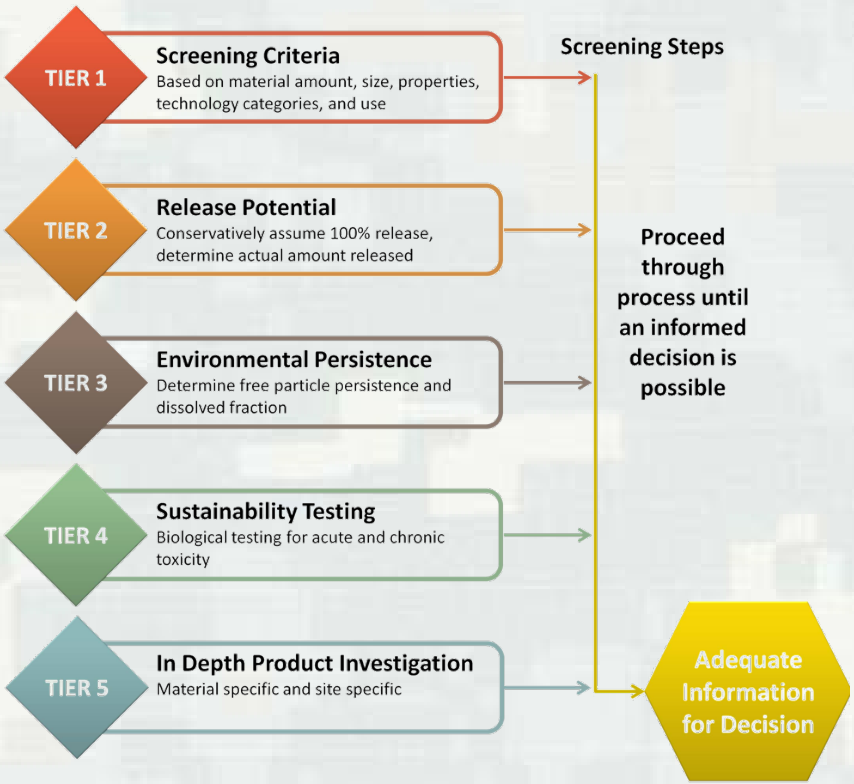
Or Google: youtube nanoexpert demo

CEA Conceptual Model Builder



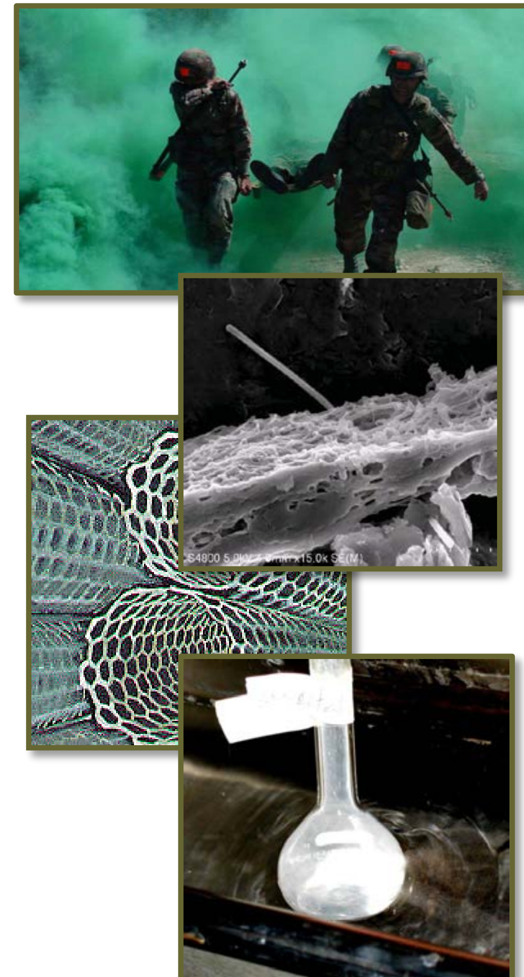
NanoGRID
(Current research program)

- Adaptive guidance framework
- Scientific methods connected to framework
- Army nanotechnology case studies (nano release?)
- Regulatory elicitation session in Feb 2015



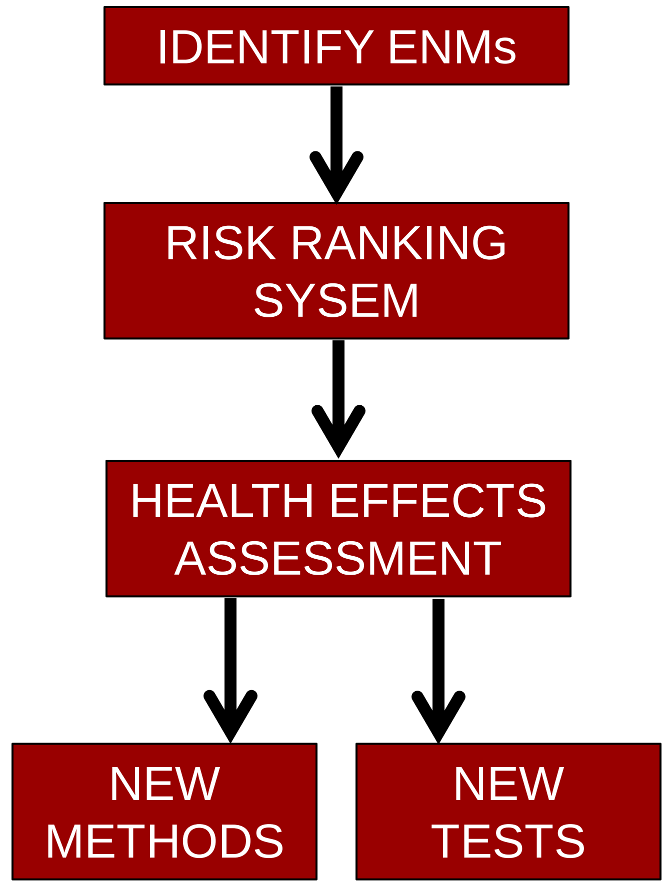
Evaluation of the Potential Medical Effects of Nanomaterials in Army Systems

- Identify engineered nanomaterials and associated Army materiel applications
- Conduct initial risk ranking of identified materiel
- *Identify research gaps and data needs*
- ***Assist the Army Public Health Command (PHC) in improving methods for evaluating the potential health risks of engineered nanomaterials used in Army materiel***
- ***Develop toxicity tests and other assessment methods necessary to support PHC health risk assessments for nanomaterials***



Approach

- **Data call** through ASA(ALT) to identify Army materiel incorporating nanomaterials
- **Extramural contract (RTI)** to provide a database and risk ranking system for Army nanomaterials associated applications
- **Partner with NIOSH** to evaluate PHC risk/health effects assessment methods
  - *Identify changes to existing approaches used for chemicals*
  - *Where necessary, **develop new toxicity tests and other assessment approaches** for nanomaterials*



Army Materiel Characteristics

Characteristics Used in Scoring	
Amount	The amount (%) of ENM incorporated into the materiel (relates to release potential, exposure potential) (e.g. a materiel containing a very small % of ENM would be less likely to release the ENM and would result in a smaller exposure concentration)
Number of End Items	The total number of individual final (produced) items for a particular ENM-application pair (relates to exposure potential) (e.g. if 5,000 end items are produced, the likelihood of exposure is greater than a materiel with currently only 2 end items)
Number of People Exposed	The total number of current individuals with the potential for exposure to the ENM-containing materiel (relates to exposure potential)) (e.g. if 3 people have the potential for exposure due to current use, rather than thousands, then exposure potential is considered low)
Acquisition Phase	The current status of the ENM-containing materiel based on life cycle stage, from concept design → production and deployment (relates to exposure potential) (e.g., a materiel that is still in the concept design phase (e.g. planning only) would have no exposure potential, whereas a materiel that has been deployed for use could potentially have a large exposure potential)
Use Patterns	A descriptor for who will primarily be using the ENM-containing materiel in its current stage and in what setting (relates to release, exposure potential, and toxicity potential) (e.g., an ENM used in an obscurant would theoretically have a higher release, exposure, and toxicity potential than an ENM used in body armor)
Incompatibility	A list of substances that may be incompatible with the ENM-containing materiel
Method of Incorporation	(Method of Incorporation): A descriptor for how the ENM is incorporated into the materiel (i.e., on the surface, in a polymer matrix, in a powder, etc.) relates to release, exposure, and toxicity potential (e.g., if the ENM is present in a polymer matrix, then the likelihood of release and subsequent exposure/toxicity would be diminished)
Characteristics Provided for Informational Purposes Only	
Toxicity Clearance	Yes/No answer on whether or not a toxicity clearance has been performed for the materiel application containing ENMs
MSDS	Yes/No answer representing the presence/absence of a material safety data sheet for the ENM used in the application
Health Hazard Assessment	Yes/No answer on whether or not a health hazard assessment has been performed on the materiel application containing the ENMs

Nanomaterial Characteristics

Chemistry
Solubility
Aggregation
Surface Chemistry

Pair-specific
Form
Shape

Fate
Dispersability
Carbon Affinity
Water Affinity
Persistence
Bioaccumulation
Degradation Potential
Half-life

Reactivity
Surface reactivity
Toxicity
Radical Formation
Catalytic Reaction
Flammability
Explosivity
Surface Charge/Zeta Potential

Structural
Particle Size
Density
Composition
Surface Area
Molecular Structure
Porosity
Crystallinity
Dustiness

Significant Data Gaps:

- 85% of database incomplete
- Size, shape, composition ENM <50%

Significant Army Assessment Gaps:

- Performed health assessment, 69%
- Presence of MSDS, 62%
- Toxicity clearance performed, 71%

Significant Usage/Exposure Data Gaps:

- 58% of database incomplete
- Method of synthesis, 12%
- Acquisition phase, 35%
- Amount of ENM, 92%
- Number of end items, 69%
- Number of people exposed, 71%
- Use patterns, 38%
- Incompatibility, 100%

Risk Ranking

$$R_{h,i,j} = \sum_{1}^{m}\left[\frac{1}{n1}\sum_{1}^{n1}(RS_{k1,m} \cdot w_{k1,m})\right] \cdot \left[\frac{1}{n2}\sum_{1}^{n2} IS_{k2}\right]$$

Total Risk Score

ENM Risk Score

Materiel Risk Score

The **Total Risk Score** = **ENM Risk Score** X **Materiel Risk Score**

The **Total Risk Score** will then be used for ranking ENM-Materiel pairs against one another.

Each ENM-specific characteristic (k1) chosen by the user from a predefined list of characteristics is associated with a Release Potential Score (RP) and/or Exposure Potential Score (EP) and/or Toxicity Potential Score (TP) in the TEARR database for a given ENM-Materiel pair and can have values of 1, 3, or 5, corresponding to low, medium, or high.

Each ENM-specific characteristic also has an associated weight (w) (user defined) with values of 0, 1, or 2.

Each RP, EP, and/or TP is multiplied by the weight for a given ENM characteristic. The weighted scores are then averaged over the total number of ENM characteristics selected (n1).

The average weighted RP, average weighted EP, and average weighted TP are then summed = **ENM Risk Score** for a given ENM-Materiel pair in the TEARR database.

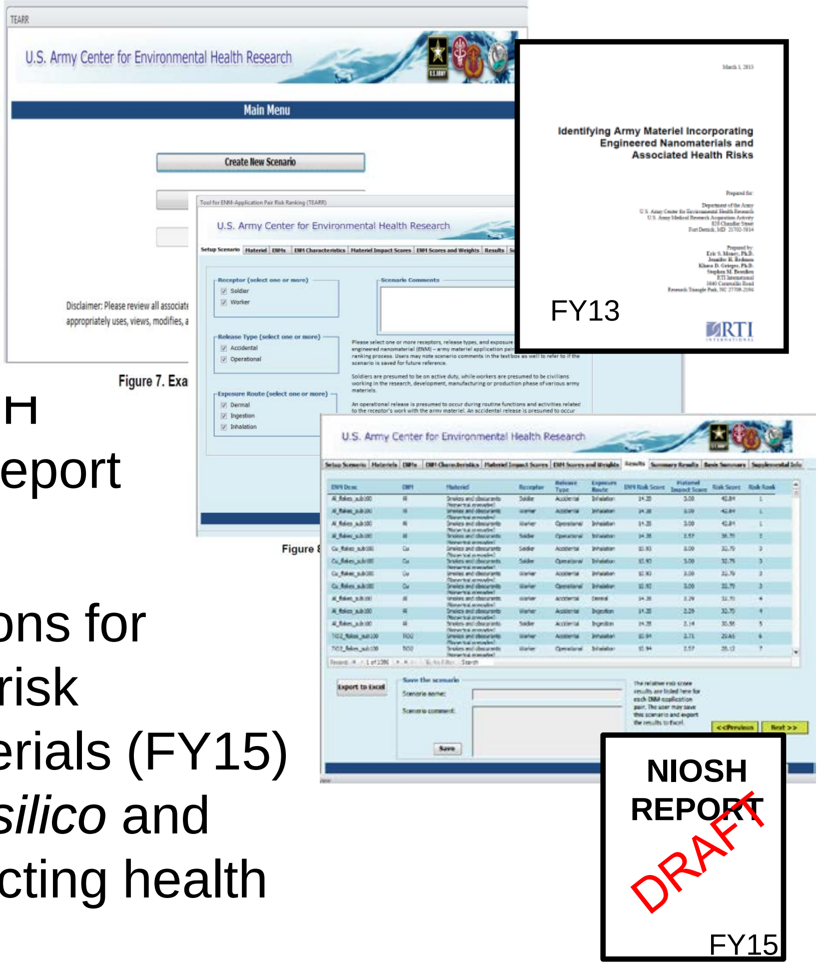
For each Army Materiel Application Specific characteristic (k2), a default impact score (IS) will be assigned in the TEARR database based on the receptor (h), release type (i), and exposure pathway (j), with values of 0, 0.5, 1, 1.5, or 2, corresponding to diminishing (0, 0.5), no effect (1), or increasing (1.5, 2) the overall risk of a given ENM-Materiel pair; however, these values can be updated by the user.

The Materiel Risk Score = the average impact score across all selected Materiel characteristics (n2).

Progress/Deliverables

- **Deliverables to date**
  - Database and risk ranking system for Army engineered nanomaterials and applications
  - Risk ranking report (133 ENM/application pairs)
- **Progress**
  - Interagency agreement with NIOSH
  - Awaiting delivery of revised draft report
- **Planned deliverables**
  - NIOSH report with recommendations for improvements to the Army health risk assessment process for nanomaterials (FY15)
  - Development and validation of *in silico* and tiered testing procedures for predicting health effects of Army ENMs

TEARR: Tool for ENM-Application Pair Risk Ranking



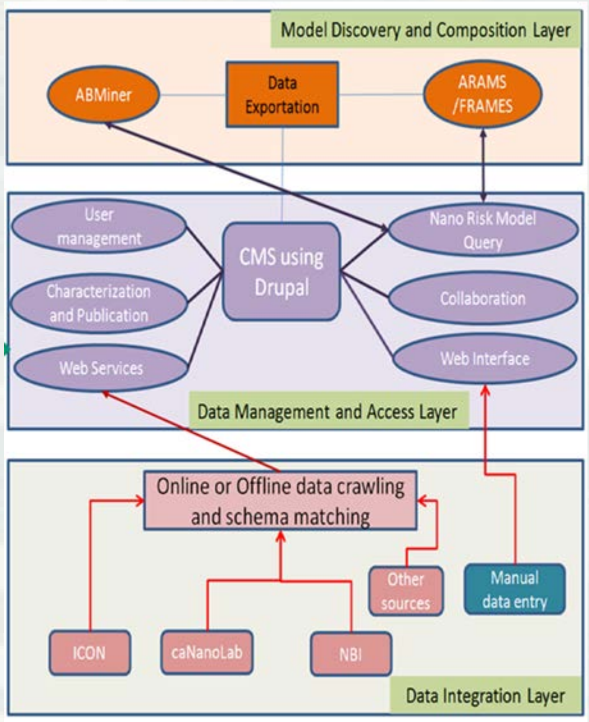
Nanomaterials: Filling the Data Gaps

- Text Mining and In-silico Approaches (Potential Research Efforts)
  - Perform network analysis of the ENM database to identify key relationships of data gaps to develop and inform text mining of open literature and searchable databases (e.g. Nanomaterial Registry)
  - Use NIOSH report recommendations to further refine and concentrate text mining data elements for further elucidation of key ENM endpoints and classifiers
  - Text mining may also provide a further refinement of toxicity endpoints and classifiers to further enhance hazard predictions of TEARR
  - Evaluate text mining outcomes to develop and validate Army-centric nano-QSAR model development and/or analysis of missing data elements

NEI Miner

SBIR with Intelligent Automation Inc

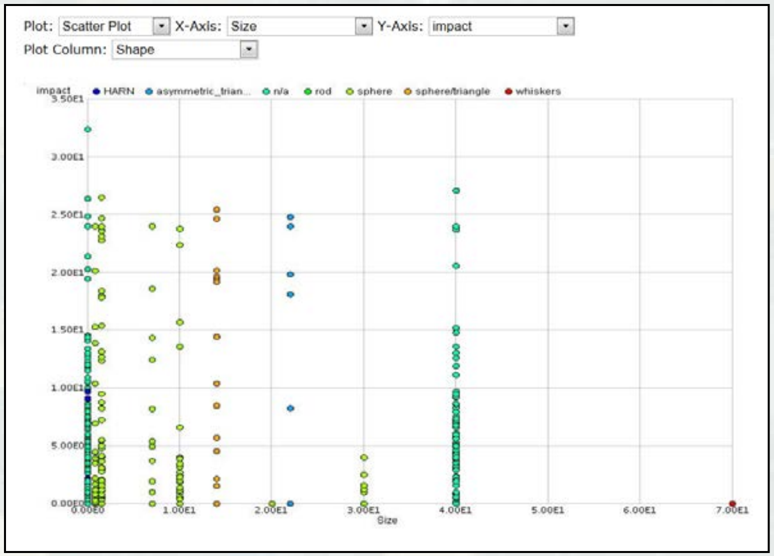
- Nanomaterial environmental impact analysis requires a comprehensive NEI modeling framework, centralized NEI database, model discovering tool and integrated model composition strategy
- 22941 entries related to nanotoxicity in the current database
- Searchable bibliography



http://neiminer.i-a-i.com

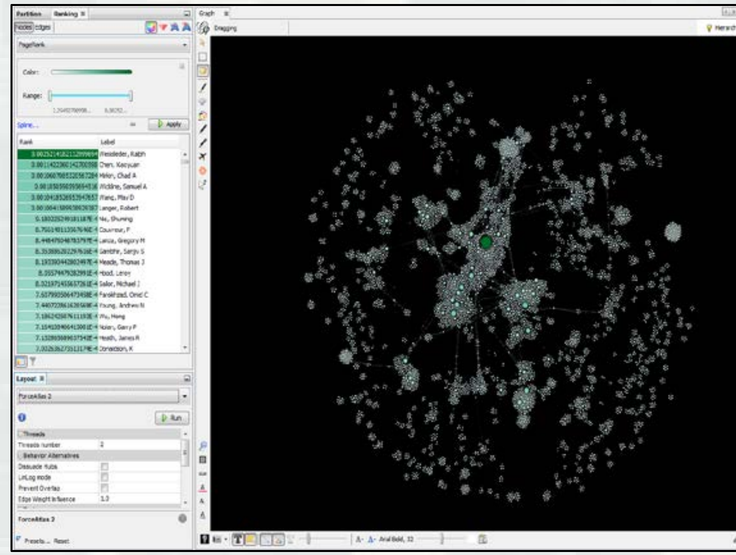
NEI Miner

Data Query Interface and Visualization



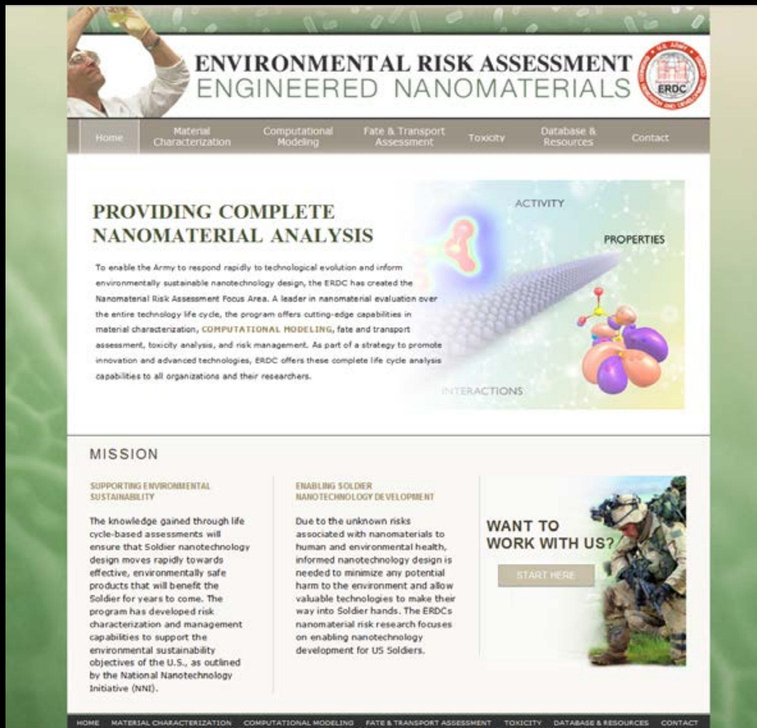
Nanomaterial Biological Interaction (NBI) Database data presented as a scatter plot.
http://nbi.oregonstate.edu/

Currently developing "prediction cube"



Galaxy plots for visualization and discovery

http://neiminer.i-a-i.com



http://el.erdc.usace.army.mil/nano/

Jeffery.A.Steevens@us.army.mil

Additional Information

Publications (2010-2013)

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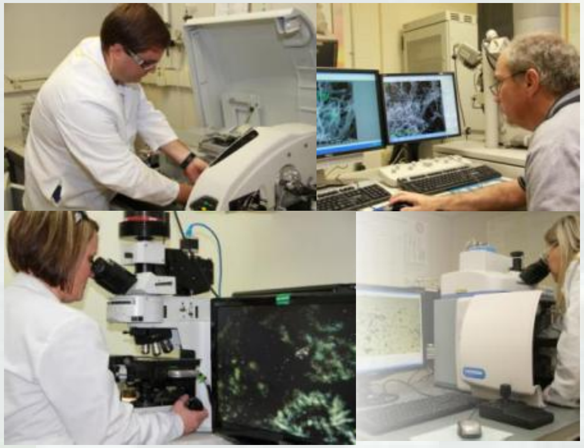
Technical Nano Team

- Toxicologists
  - Ms. Jessica Coleman, Dr. Keri Donahue, Dr. Kurt Gust, Mr. Al Kennedy, Dr. Jacob Stanley, Dr. Jeffery Steevens
- Risk and decision science
  - Mr. Matthew Bates, Mr. Zach Collier, Dr. Igor Linkov
- Chemists / geochemists
  - Dr. Anthony Bednar, Dr. Mark Chappell, Mr. Chris Griggs, Dr. Fran Hill
- Material Scientists / characterization
  - Dr. Michael Cuddy, Dr. Robert Moser, Dr. Aimee Poda, Dr. Charles Weiss
- IT / informatics
  - Dr. Amy Bednar
- Technical directors offices
  - Mr. Ryan Carbone, Dr. Elizabeth Ferguson



Capabilities/Testing

- Multidisciplinary: EL, GSL, ITL
- Ecotoxicology:
  - Water, sediment, soil bioassays
  - Environmental chambers
  - Flow through / diluter boards
  - Digital tracking
  - Respiration
  - Histology
- Material Characterization:
  - State of art characterization equipment and facilities
  - Durability testing / weathering
  - Subject matter experts
  - Mechanical properties
- Analytical Chemistry:
  - Standard materials analysis and research chemistry
  - Detection of compounds in environmental matrices

Instrumentation

- AFM
- Centrifuge (ultra)
- Confocal microscopy
- Disk Centrifuge
- Dynamic light scattering
- Electrophoretic mobility, autotitrator
- E-SEM / EDX/EDSD/STEM
- FFF-ICP-MS
- FTIR
- Hyperspectral microscopy
- ICP-MS, GFAAS
- Nanoindentation
- NanoSight
- NMR
- Quartz crystal microbalance
- RAMAN Spec
- Universal testing machine
- UV-vis / NIR (high res)
- X-ray tomography
- XRD/XRF
- Nano Calorimeter