Sediment and Terrestrial Toxicity and Bioaccumulation of Nano Aluminum Oxide

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**Report Documentation Page**

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Standard Form 298 (Rev. 8-98)

Prescribed by ANSI Std Z39-18
Research Team

Dr. Jacob K. Stanley, Research Biologist
Dr. David R. Johnson, Research Biologist
Dr. Anthony J. Bednar, Research Chemist
Dr. Charles A. Weiss, Jr., Material Scientist
Dr. Jeffery A. Steevens, Research Toxicologist
Risk Assessment of Nanomaterials

- Identify and quantify environmental attributes of nanomaterials
  - Sources?
  - Fate and transport mechanisms?
  - Likely exposure scenarios?
  - Biological effects?

- Characterize physical / chemical interactions between engineered nanomaterials and environmental media

GOAL → Establish approaches for predicting relevant characteristics associated with toxicity and environmental impacts (persistence, fate, toxicology)
ERDC Nanomaterials Risk Research Cluster

- Material characterization
- Fate and transport
- Ecotoxicology
- Computational chemistry
- Risk and decision analysis

Interdisciplinary team of experts in fields of materiel science, geology, soil science, toxicology, and computational chemistry
Conceptual Model: Environmental Impact of Nanomaterials

1. Sources
   - Engineered Nanostructures
   - Engineered Nanodevices
   - Reaction Intermediates
   - Production Waste
   - Product Degradation

2. Media and Transport Processes
   - Air
     - Aggregation/UV Degradation
   - Settling/suspension
   - Soil
     - Degradation
   - Sorption/desorption
   - Water
     - Aggregation/Degradation
   - Settling/suspension
   - Sediment
     - Degradation

3. Exposure Pathways and Receptors
   - Terrestrial Vertebrates
   - Terrestrial Invertebrates
   - Aquatic Invertebrates
   - Fish
   - Benthic Invertebrates
Current Research Materials

- Silver
- Fullerene
- Aluminum Oxide (Al₂O₃)
- MWCNT
Nano Aluminum

Potential military uses:

- Oxidizer in energetics / propellants
  - High energy release during oxidation to Al₂O₃
  - Diesel fuel additive (Tyagi et al. 2008) in rocket propulsion
- Increase burning rate, heat, and energy density
  - Lower ignition time
  - Reduces ignition time and temperature by two-fold (Armstrong et al. 2003; Meda et al. 2007).

Industrial uses:

- Coatings
- Abrasives
- Polishing of optics and jewelry

All create potential sources of release for nano Al₂O₃ to environment
Assessing Impact of Nano $\text{Al}_2\text{O}_3$

- Need to assess both human and environmental impact.

- Arising regulatory requirements could limit military use if not extensively characterized; i.e. European Union on the Registration, evaluation, Authorization and Restriction of Chemical substances (REACH).

- Aim to follow a comprehensive environmental assessment (CEA); provides holistic outlook on material life cycle and environmental risk.

- New DoD technologies undergo an technology development and acquisitions process; track R&D, production, deployment, use and disposal.
Stages of Acquisition Process Benefiting from Environmental Hazard Assessment

Technology development and acquisitions process. Adapted from Mike McDevitt, Installations Management Command
Environmental Risk of Nano Al₂O₃

• What are the potential environmental risk of nano Al₂O₃ particle release?

• Due to use of material over land ranges and potential for water runoff and soil mobility, how do factors such as fate, transport in terrestrial and aquatic environments affect organisms?

Use in additives/explosives/propellants

Nano Al₂O₃ particles dispersed

Potential impact on terrestrial/aquatic organisms
Case Study: Nano Al₂O₃ in Terrestrial Systems

1. Sources
   - Engineered Nanostructure
   - Engineered Nanodevices
   - Reaction Intermediates
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   - Product Degradation

2. Media and Transport Processes
   - Air
     - Aggregation/UV Degradation
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     - Settling/suspension

3. Exposure Pathways and Receptors
   - Terrestrial Vertebrates
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   - Benthic Invertebrates

Deposition, Spills
Intentional application
Model Species: *Eisenia fetida*

- **Habitat:** upper layers of soil
- **Ecological impact:** nutrient cycling and food source for larger predators

**Rationale for exposure of *Eisenia fetida* to nano **Al**$_2$O$_3$**:
- Earthworms imbed in soils $\rightarrow$ potential for whole body exposure
- Earthworms exhibit toxicity response to certain metals
- Potential for bioaccumulation through ingestion and dermal uptake
Experimental Approach

28-Day Sub-Chronic Bioaccumulation/Toxicity Study:

*E. fetida* exposed to a nano and micron-sized $\text{Al}_2\text{O}_3$ treated soil

Soil Avoidance Bioassay:

48-hour soil avoidance study exposing earthworms to nano and micron-sized $\text{Al}_2\text{O}_3$ amended soils utilizing a soil avoidance wheel.
Nano Al₂O₃ Characterization

Nano Al₂O₃

• TEM Image
• Particles 1->100nm present, manufacturer size 11nm
• Spherical particles and rods present
• DLS- bimodal populations
• Zeta potential- not stable in water

Micron-sized Al₂O₃ SEM Image
• Consistent with manufacturer statement, Al₂O₃ particles between 50-200 µm
Sub-Chronic Bioaccumulation Toxicity Study: Soil Exposures

Earthworms depurated 24-hours
Adults 0.3-0.6 g

10 added per treatment

Test conducted 28-days at 22°C, 80% humidity, continuous light

Endpoints assessed: bioaccumulation, toxicity, growth, reproduction

Treatments 0-10,000 mg/kg
Results

Bioaccumulation

Reproduction

100% survival, but reproductive toxicity observed
Soil Avoidance Results: 48-h

![Image of soil samples](image)

**Graph:**
- **Y-axis:** Ratio of 10 = 100% of earthworms recovered in control soil
- **X-axis:** Nominal Al Soil Concentrations mg/kg
- **Legend:**
  - Nano
  - Micron-sized

- Nominal Al Soil Concentrations mg/kg:
  - 625
  - 1250
  - 2500
  - 5000
  - 10000

- **Legend Notes:**
  - * indicates a statistically significant difference.
Discussion: Terrestrial Impact of Nano Al₂O₃

- Nano Al₂O₃ may cause negative impacts in terrestrial invertebrate populations such as reduced reproduction and habitat.
- Negative impacts only observed at > 3,000 mg/kg nano Al₂O₃.
- Concentrations where effect is observed is unlikely to be found in the environment except under extreme circumstances.

Case Study: Nano Al$_2$O$_3$ in Aquatic systems

1. Sources
   - Engineered Nanostructure
   - Engineered Nanodevices
   - Reaction Intermediates
   - Production Waste
   - Product Degradation
   - Deposition, Spills
   - Intentional application

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   - Terrestrial Invertebrates
     - Contact, Ingestion
   - Aquatic Invertebrates
     - Contact, Ingestion
   - Fish
     - Ingestion
Organisms Tested

- **Tubifex tubifex**
- **Hyalella azteca**
- **Lumbriculus variegatus**
- **Corbicula fluminea**
**Nano Al₂O₃ Sediment Tests - Survival**

**Survival up to 100,000 mg/kg**

**Tubifex tubifex**

Significant mortality at 2500 mg/kg in sediment

**Hyalella azteca**

**Mean proportion survival**

<table>
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<th>Al₂O₃ treatment</th>
<th>Control</th>
<th>625 mg Bulk</th>
<th>625 mg Nano</th>
<th>2500 mg Bulk</th>
<th>2500 mg Nano</th>
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<tr>
<td>Proportion Survival</td>
<td>1.0</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
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Nano Al₂O₃

Micron-sized Al₂O₃
Bioaccumulation factor (BAF)-ratio of the contaminant in an organism to concentration in environment at steady state.

**28-d Nano Al₂O₃ Sediment Bioaccumulation**

Bioaccumulation factor (BAF) - ratio of the contaminant in an organism to concentration in environment at steady state.

**Treatment**

25g/kg Al₂O₃

**Lumbriculus variegatus**

**Corbicula fluminea**

BAF (tissue Al/sediment Al)
Hyalella azteca 10-d - Bioaccumulation

![Bioaccumulation Factor (BAF) graph]

- **Bulk Al₂O₃**
- **Nano Al₂O₃**

<table>
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<tr>
<th>Al₂O₃ Treatment Level</th>
<th>Bioaccumulation Factor (BAF)</th>
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<tbody>
<tr>
<td>Control</td>
<td>0.16</td>
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<td>10000</td>
<td>0.12</td>
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<td>25000</td>
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<td>50000</td>
<td>0.04</td>
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<td>100000</td>
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Confocal Image

Hyalella azteca
Discussion – Aquatic Exposures

• No toxicity observed to *Tubifex*
• Nano more toxic than bulk to *Hyalella*
• BSAFs similar for nano and bulk in *Hyalella* and *Corbicula* bioaccumulation studies
• BSAF for bulk higher than nano in *Lumbriculus*
• However, significant effects observed only at high, environmentally unrealistic concentrations
• Therefore, our results support a finding of low environmental risk of nano Al₂O₃ to benthic and terrestrial invertebrates

Stanley et al 2010. Sediment toxicity and bioaccumulation of nano and micron-sized aluminum oxide
Steps Forward: Incorporate into Comprehensive Environmental Assessment (CEA)

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<th>Life Cycle Stages</th>
<th>Environmental Pathways</th>
<th>Fate &amp; Transport</th>
<th>Exposure – Dose</th>
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<td>Air</td>
<td>Primary contaminants</td>
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Analytical methods development and application

Adapted from Davis, 2007
To learn more about the nano CEA:

# 12667 A Comprehensive Environmental Assessment Approach to Making Informed Decisions about Engineered Nano Particles

Dr. David Johnson
Thursday, 2:30
Room 278
US Army Engineer Environmental Laboratory, Vicksburg, MS, USA

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