Missouri Waste Control Coalition Conference (2018):
Thinking Small: The Growing Presence of Engineered Nanoparticles in Wastewater
July 16, 2018

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OVERVIEW

Background
- Nanoparticle characteristics
- Types of nanoparticles

Nanoparticle Applications
- Examples of everyday use
- Benefits of nanomaterials
- How much is being released
- Environmental transport
- Impacts on activated sludge process; biofilms
- Occurrence in solid waste; leachate

Environmental Quantities

Wastewater interactions

Regulatory Compliance
- US FDA Guidance documents
- CERCLA, RCRA, TSCA, FIFRA, FFDCA
WHAT ARE NANOPARTICLES?

**Engineered nanoparticles AKA ENPs:**
Less than 100 nm
Well dispersed and stabilized with a shell material
High specific surface area -> increased reactivity
INCREASED REACTIVITY

SIZE EFFECTS

Aggregation
- Strongly bonded interactions
  - Irreversible

Agglomeration
- Weakly bonded interactions
  - Reversible

Interact with Surrounding Environment

Oxidation
Adsorption of Compounds
Dissolution
Redox
ROS Generation (free radicals)

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Aggregation/Agglomeration are controlled through:

- **Structural Characteristics**
  - Surface Functionalization
  - Major factor in flocculation and removal efficiency

- **Surrounding Environment**
  - Presence of Organics
  - Reduces coagulation by adsorption to ENP surface

Images courtesy of google images
TYPES OF NANOPARTICLES
Metal Oxides

Titanium Dioxide
Examples with ~1 ug Ti/mg Food
- Mentos Freshmint Gum
- Hostess Powdered Donuts
- Kool Aid Blue Raspberry
- M&M’s Chocolate Candy
- Betty Crocker Whipped Cream Frosting

Zinc Oxide
TYPES OF NANOPARTICLES
Metals

Gold

Au-NP Applications
Chemotherapy (Drug Delivery)
Biosensors
Gene Delivery

Silver
Where are Engineered nanoparticles?

Applications include:
Dispersion in gels
Attachment to surfaces
Embedded in polymers
Applied in industrial processing

Toiletries (deodorant, toothpaste, face washes/creams)

Drug delivery, antibacterial, medical supplies

Carpets, toys, clothing (self cleaning or antibacterial surface coatings)

Images courtesy of google images
## ENVIRONMENTAL QUANTITIES

<table>
<thead>
<tr>
<th>Industry</th>
<th>Quantity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile industry</td>
<td>2.6-6.3 Megagrams in one year</td>
<td>(silver nanoparticles)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1 Mg ~ 1.1 U.S. Tons)</td>
</tr>
<tr>
<td>Sunscreen industry</td>
<td>14.3 – 143 Mg in 2008</td>
<td>(titanium nanoparticles, GLOBALLY)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1 Mg ~ 1.1 U.S. Tons)</td>
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</tbody>
</table>

**Titanium Dioxide (TiO2)**

- **34,000 Megagrams production total** in one year (75 million pounds) **U.S. ONLY**
- **19,000 Mg released** TCE reported (1994) (42 million pounds)
ENVIRONMENTAL CONCERNS

Bioaccumulation of Silver through ingestion of algae in *Daphnia magna* (zooplankton)

**Clean Water Act – Acute Toxicity**

Silver ion toxicity *Thalassiosira weissflogii* (marine diatom)

Decreased leaf litter decomposition rates by freshwater bacterial communities

Pradhan et al. 2011
Burchardt et al. 2012
ENVIRONMENTAL CONCERNS

Toxicity and bioaccumulation of nano-TiO₂

Chronic doses as low as 5 mg/kg in mice show liver damage, impairment of spatial recognition, accumulation in intestines

Negative toxicological effects to macroinvertebrate community structure under chronic exposure to 25 mg/kg

Jovanović, B. 2015
TRANSPORT OF NANOPARTICLES

Nanowaste
  - POTWs
    - Soil
  - Landfills
    - Water
    - Leachate
FATE & TRANSPORT IN TREATMENT WORKS

Collection System
- Potential for chemical speciation; sorption to suspended solids or biofilm

Primary Treatment
- Potential removal through sorption, aggregation

Aeration Basin (Activated Sludge)
- Microbial uptake; entrapment; complexation with organic matter

Secondary Clarifier
- Sedimentation by adsorption to floc

Biosolids Processing
- Chemical speciation and complexation with organics; potential for dissolution after land application

Attached Growth Reactor
- EPS encapsulation; retention and release; microbial uptake; complexation with organic matter

Secondary Clarifier
- Sedimentation by adsorption to detached biofilm

Disinfection
- Increased oxidation and toxicity

Effluent to nearest waterway
- Release of Me(O)NPs through dissolution, unsettled suspensions

Image: Walden and Zhang, 2016
REMOVAL AND CHALLENGES IN TREATMENT WORKS

Biological Treatment
- Activated Sludge: 90-99% removal
- Attached growth (Biofilm): few studies, 10%

Source Control
- Commercially uncontrolled
- Enters water system through abrasion, disposal, and/or application

Toxicity
- Silver is more toxic when dissolved
- Ciliates, methanogens, *Nitrosomonas europaea* activity, intact RBC biofilm

Images courtesy of google images
Metal Pollutants included in Part 503 Biosolids Rule

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Ceiling concentration (milligrams per kilogram)</th>
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<td>Arsenic</td>
<td>75</td>
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<tr>
<td>Cadmium</td>
<td>85</td>
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<tr>
<td>Copper</td>
<td>4300</td>
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<td>Lead</td>
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<td>Mercury</td>
<td>57</td>
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<tr>
<td>Molybdenum</td>
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<tr>
<td>Nickel</td>
<td>420</td>
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<tr>
<td>Selenium</td>
<td>100</td>
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<tr>
<td>Zinc</td>
<td>7500</td>
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</tbody>
</table>

The estimated concentrations in sludge-treated soils:

- nano-TiO₂ ~ 42 μg/kg/year
- Ag-NPs ~ 662 ng/kg/year

Concerns:

- Eco-toxicological risks
- Soil Runoff
- Uptake by plants -> bioaccumulation
INDIRECT POTABLE REUSE

Orange County, CA
• Treated wastewater replenishes groundwater

Groundwater Treatment
• Advanced Treatment: Ultrafiltration; Reverse Osmosis

Worst Case
• 0.04 ppb Ag-NPs
• 147 ppb TiO$_2$
• 0.28 ppb ZnO

Berlin, Germany
• Treated wastewater replenishes groundwater

Groundwater Treatment
• No Advanced Treatment

Worst Case
• 3.3 ppb Ag-NPs
• 13 ppb TiO$_2$
• 0.25 nano-ZnO

Kirkegaard et al. 2015
‘NANO-WASTE’ REGULATIONS

US Regulations
- TSCA
- FDA (guidance docs)
- FIFRA

European Union
- REACH

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‘NANO-WASTE’ REGULATIONS

TSCA (40 CFR 704.20; 2017) applies to:

- Chemical Manufacturing or Processing (NAICS codes 325).
- Synthetic Dye and Pigment Manufacturing (NAICS code 325130).
- Other Basic Inorganic Chemical Manufacturing (NAICS code 325180).
- Rolled Steel Shape Manufacturing (NAICS code 331221).
- Semiconductor and Related Device Manufacturing (NAICS code 334413).
- Carbon and Graphite Product Manufacturing (NAICS code 335991).
- Home Furnishing Merchant Wholesalers (NAICS code 423220).
- Roofing, Sliding, and Insulation Material Merchant Wholesalers (NAICS code 423330).
- Metal Service Centers and Other Metal Merchant Wholesalers (NAICS code 423510).
‘NANO-WASTE’ REGULATIONS

FIFRA (section 3g) applies to:

- the registration, distribution, sale, and use of pesticides in the United States.

Nanosilver pesticides
Examples: AGS-20 and NSPW

Products such as trash cans, cell phones, computers, furniture, watch bands, uniforms, sportswear, or office supplies that have labels claiming that the products are “antimicrobial” or “antibacterial”

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‘NANO-WASTE’ REGULATIONS

Other site specific applications:

- CERCLA, RCRA
- FFDCA
- CWA CAA
- National Nanotechnology Initiative
- Consumer Product Safety Commission

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QUESTIONS?

COMMENTS?

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