Nanotechnology and the Environment

MWRDGC

26 June 2009

Kathleen Sellers, PE

kate.sellers@arcadis-us.com

Agenda

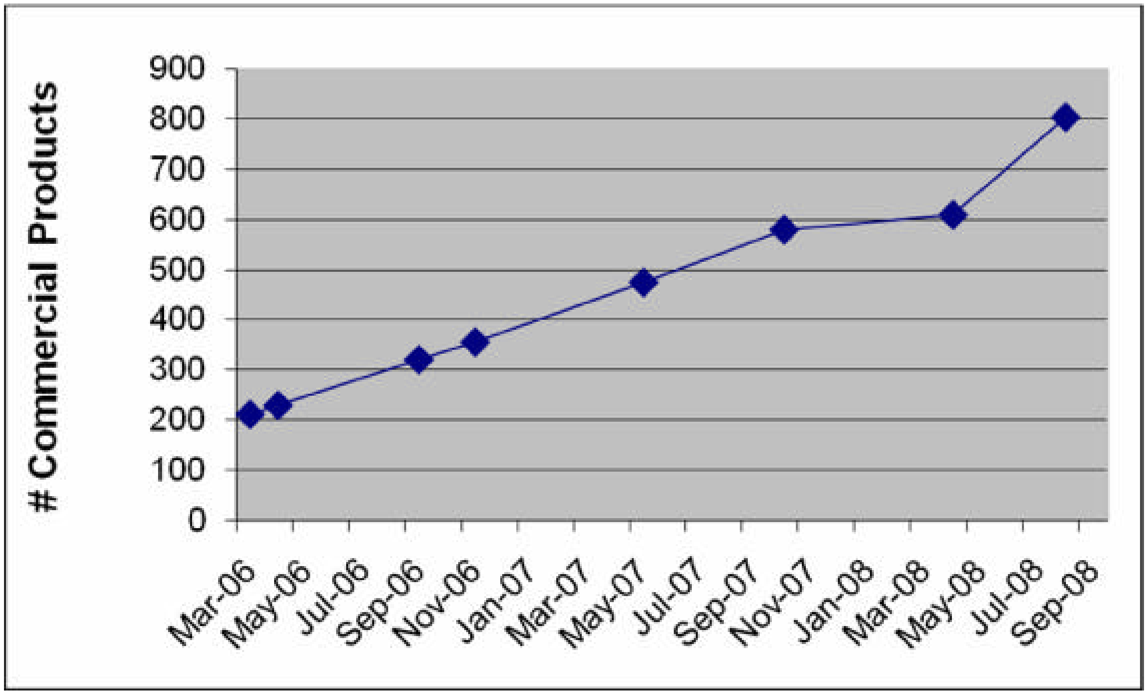
1. Safety moment
2. Terminology, basic principles, and applications
3. Fate and transport of nanomaterials in the environment
4. Potential human health risks
5. Case study: nanosilver and wastewater treatment
6. Summary and conclusions

Why are we talking about this?

- By one estimate, could grow to $3.1 trillion share of the global marketplace by 2015.

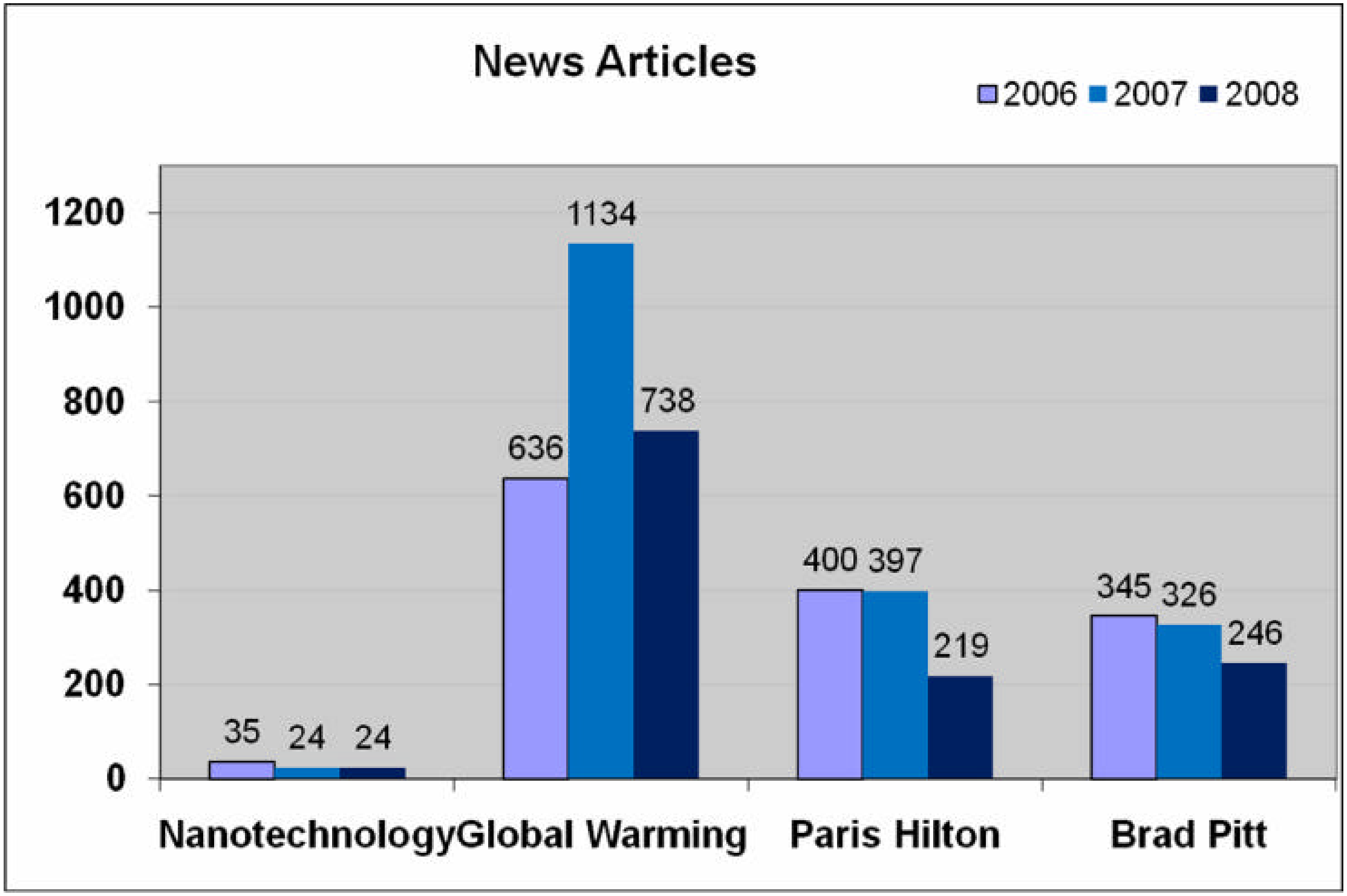
- Not a single monolithic industry, but technology that affects multiple industries.

- 3-4 new products reaching the market every week (2008 estimate).



Data from www.nanotechproject.org

Why haven't we heard about this before?



Data obtained from keyword search of Newsbank database (America's News Magazines) 01/16/09

Nanotechnology in the news

"A recent study has found that consumer products that contain silver nanoparticles may be destroying good bacteria used for wastewater treatment"

» KMWU radio, May 2008

"In Study, Researchers Find Nanotubes May Pose Health Risks Similar to Asbestos"

» New York Times, May 2008

"Skin Deep – New Products Bring Side Effect: Nanophobia"

» New York Times, December 2008

TERMINOLOGY AND BASIC PRINCIPLES

Nanotechnology is….

"… research and technology development at the atomic, molecular, or macromolecular levels using a length scale of approximately 1 to 100 nanometers in any dimension; the creation and use of structures, devices, and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on an atomic scale."
[USEPA, Feb 07]

Nanometer = one–*billionth* of a meter.

ARCADIS

One nanometer (or one-billionth of a meter) means…

Earth is approximately 10^8 times larger than a soccer ball. This same ratio describes the difference in size between the soccer ball and a nanoparticle of carbon (C60), approximately 0.7 nanometers (nm) in diameter.

Photo of a fullerene by Luann Becker. From http://nai.arc.nasa.gov/news_stories/news_detail.cfm?ID=40

Properties

Nanoparticles have different properties than bulk materials due to:

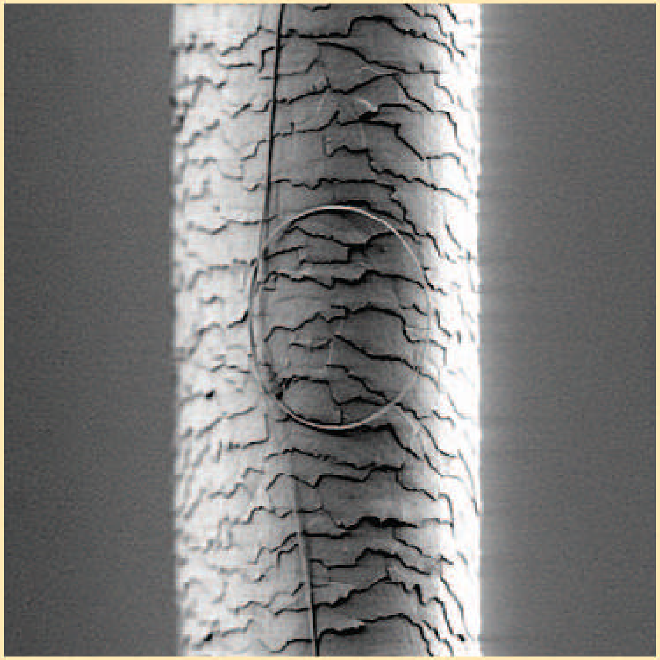
- Increased relative surface area per unit mass, which increases chemical reactivity.

- The influence of quantum effects at the nanometer size, which changes essential material properties (optical, magnetic, and electrical properties).

I think I can safely say that nobody understands quantum mechanics."

\- Richard Feynman

Types of Nanomaterials



For comparison's sake. A micrograph shows a nanowire curled into a loop in front of a human hair. Nanowires can be as slender as 50 nanometers, about one-thousandth the width of a hair.

Photo by Limon Tong/Harvard University

http://www.nsf.gov/od/lpa/news/03/pr03147_images.htm

- Naturally occurring
  - Examples: Volcanic ash, diesel emissions (soot), viruses
- Man-made
  - Composition (metal, carbon)
  - Shape
  - Size
  - Surface area / activity
  - Fixed vs free

Applications and "Common" Types of Nanomaterials

Structure	Carbon Based		Metal-based	
Particle	Carbon black	pigment, rubber	TiO_2	cosmetics, remediation
			nZVI; Fe_3O_4	remediation
			Ag	antibacterial
Tube/wire	Nanotube	electronics, sporting goods	Nanowire	electronics
Dendrimer	G5 dendrimer	drug delivery	FeS in dendrimers	remediation
Other	Fullerene	cosmetics	Quantum dots	semiconductor

Critical characteristics

(SCENIHR, 2009; OECD 2008)

Physical properties

- Size, shape, specific surface area, aspect ratio
- Agglomeration/aggregation state
- Size distribution
- Surface morphology/topography
- Structure, including crystallinity and defect structure
- Solubility

Chemical properties

- Structural formula/molecular structure
- Composition of nanomaterial (including degree of purity, known impurities or additives)
- Phase identity
- Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential)
- Hydrophilicity/ lipophilicity

Properties of the same nanomaterial vary

- **Properties can vary** depending on
  - Manufacture/batch, including
    - Particle size/ range of sizes
    - Impurities
    - Surface coatings/functionalization
  - Point in life cycle

- Lack of reference materials

- Consequence: **challenge for understanding fate and transport and toxicity mechanisms**; difficulty in extrapolating test data

How much do we know about the properties of nanomaterials?

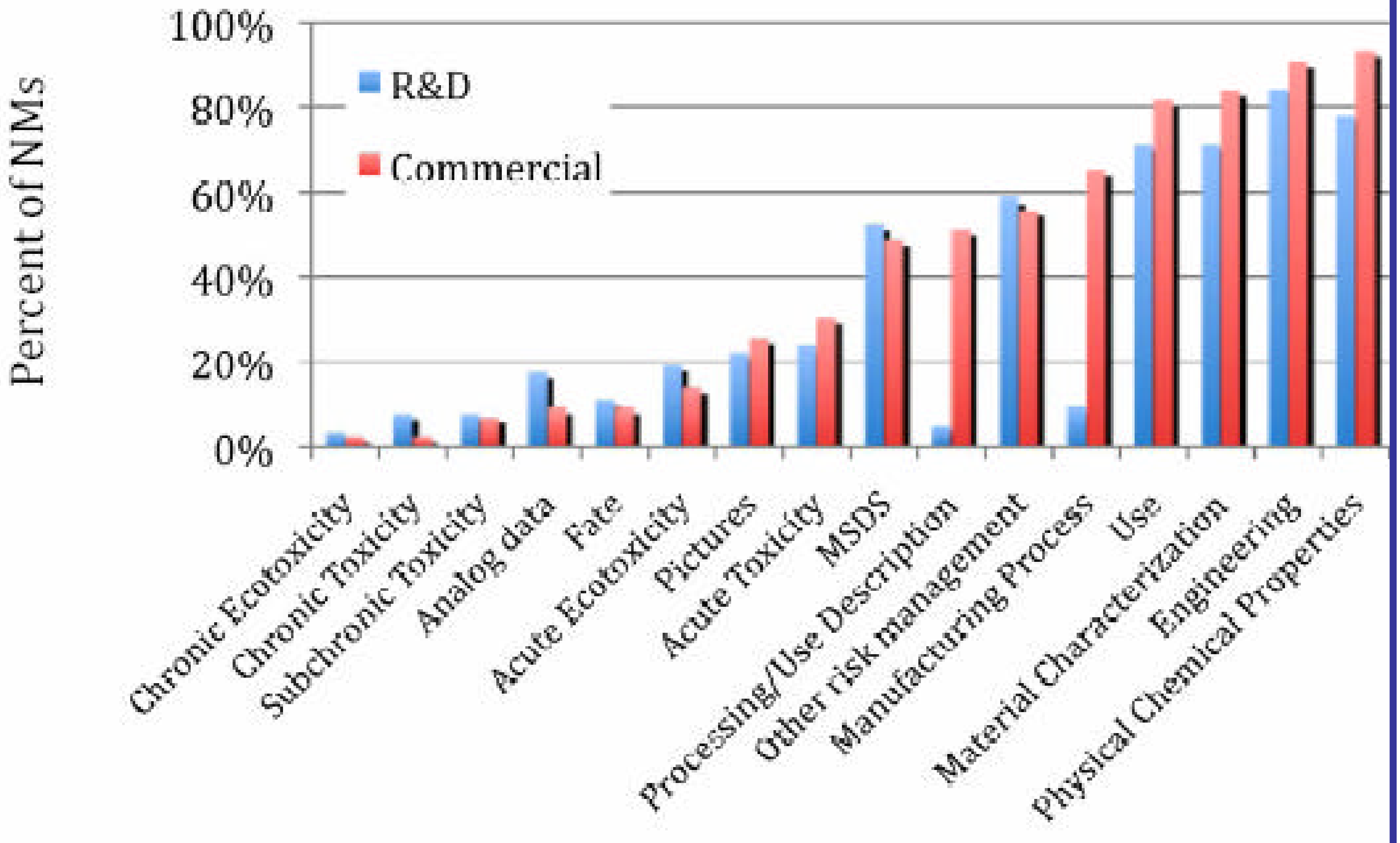


Figure 4 Submissions of nanoscale material (NMs) to the NMSP by inclusion of data for a particular element

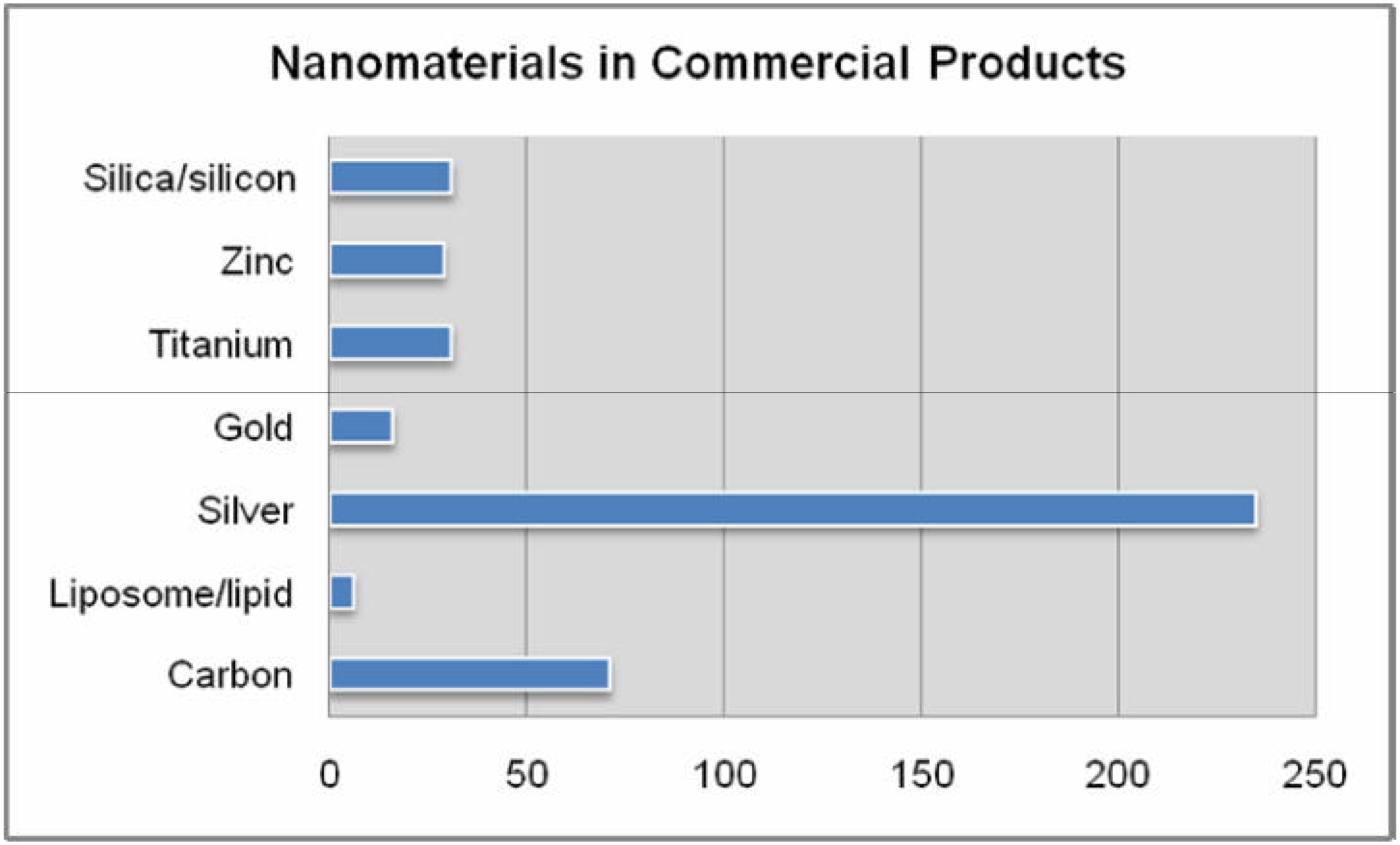
U.S. EPA, 2009

Commercial Uses of Nanomaterials

PRODUCT CATEGORY	% OF TOTAL	EXAMPLE	NANOMATERIAL
Appliances	4%	DeWalt cordless power tool	phosphate nanocrystal battery
Automotive	5%	Envirox™ Fuel Borne Catalyst	cerium oxide
Cross-cutting	6%	Antibacterial door lock	nano silver
Electronics/ Computers	7%	Invisicon® computer screen	carbon nanotube
Food and Beverage	10%	Beer bottle plastics (Miller Brewing)	nano clay particles
Goods for children	2%	Benny the Bear plush toy	nano silver
Health and Fitness	63%	DoubleL® Chinos	Nano-Care® by Nano-Tex
Home and Garden	11%	Pilkington Active™ self-cleaning glass	nano titanium dioxide?
Medical applications	2%	Doxil® anti-cancer drug	lipid nanoparticles w/ PEG coating

Data obtained from product inventories maintained by The Project on Emerging Nanotechnologies (http://www.nanotechproject.org/inventories/) 08/21/08

Major Materials



Data obtained from product inventories maintained by The Project on Emerging Nanotechnologies (http://www.nanotechproject.org/inventories/) 09/28/08

Hype vs Hope
Part I: Possible Benefits

<u>Energy savings</u> – could reduce energy consumption substantially

<u>Alternative energy supplies</u> – decrease cost of solar panels; advances in battery technology; hydrogen fuel cells.

<u>Efficient use of raw materials</u> – decrease mass of catalysts used; increase rate of production and decrease waste generation.

<u>Environmental protection</u> – treatment of air, wastewater, and groundwater; environmental sensors.

<u>Medical breakthroughs</u> – imaging; targeted drug delivery; artificial bone; sensors.

Hype vs Hope
Part 2: Possible Benefits?

Benny the Bear Plush Toy

"Pure Plushy combines the use of Memory Foam and Silver Nanotechnology to form the perfect stuffed toy for children with allergies!"

Hay Fever Sufferers-Rejoice! New Nano-Coats in Japan Can Repel Pollen

Japanese apparel manufacturer Sanyo Shokai recently released a men's coat that is both pollen and water-resistant, using Toray's proprietary textile nanotechnology fabric-NanoMATRIX."

Nano Pacifier

FATE AND TRANSPORT

Not all nanomaterials are created equal

- Nanomaterial products can vary between manufacturers and batches with respect to:
    - Size (nominal and range of particle sizes)
    - Impurities
    - Functionalization

- These variations affect behavior and toxicity.

- Variability can limit generalizations about a specific nanomaterial.

Potential for Exposure

Point in Life Cycle:	Synthesis	Product Manufacture	Consumer Use	Disposal
Potential Exposures:	•Workers •Air/ water discharges	•Workers •Air/ water discharges	•Direct exposure	•Workers •Wastewater •Landfill •Recycling

ARCADIS

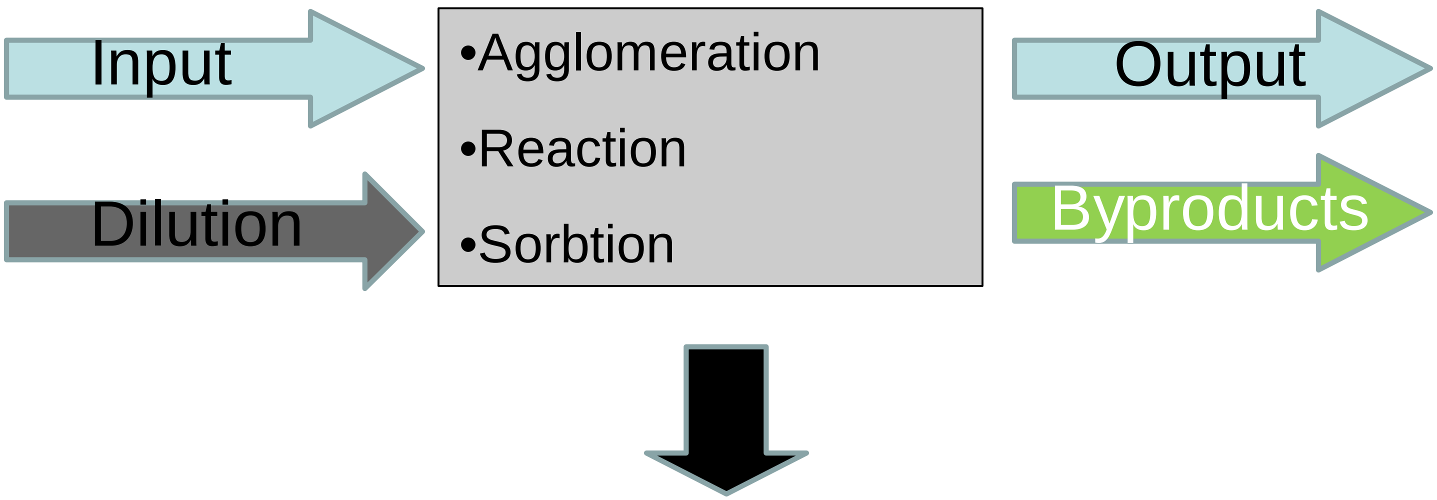
Degree of Exposure

Consider the source:

Free vs fixed

Mass balance

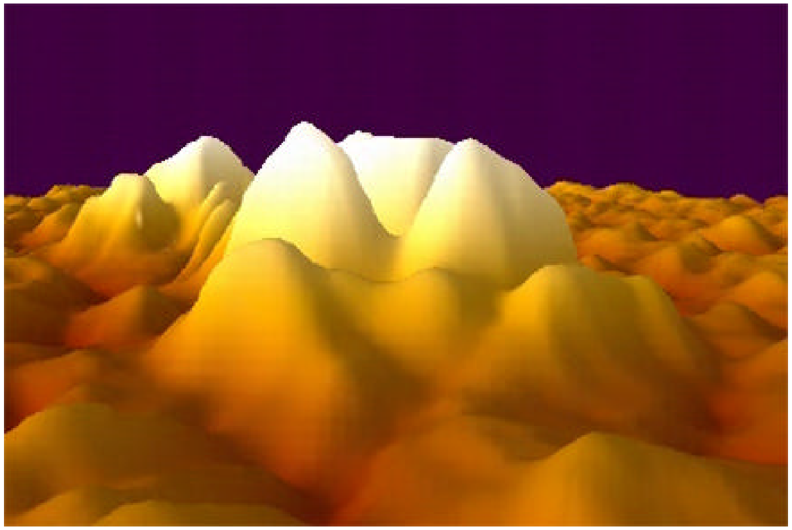
Fate and transport in the environment



Degree of exposure typically cannot be readily measured

- No off-the-shelf technology yet to identify and quantify nanoparticles in environmental samples.

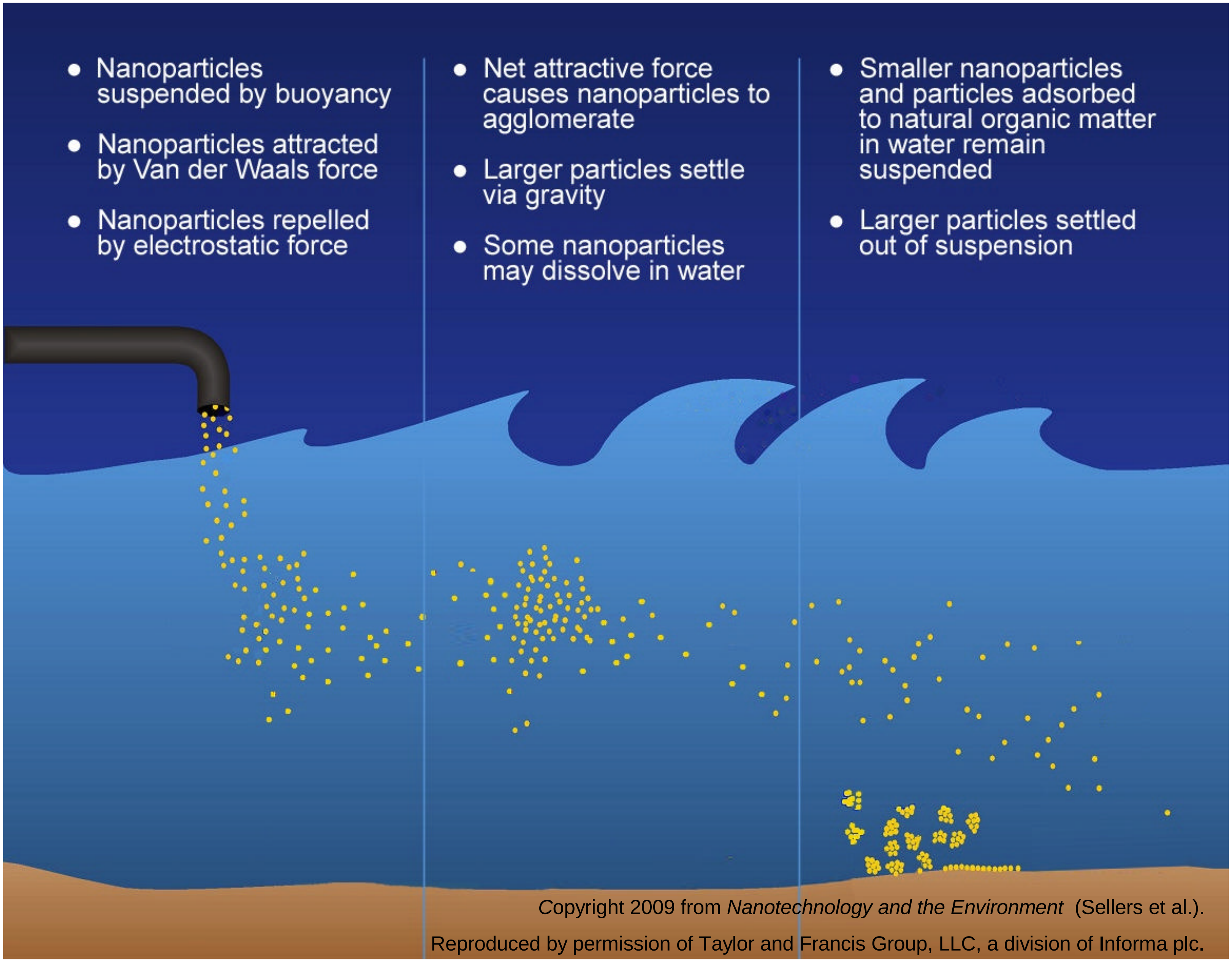
- Challenge: distinguishing nanoparticles from naturally occurring material.



TM Image of Fullerenes

(From *Nanoscience Instruments* http://www.nanoscience.com/education/gallery.html)

Environmental Fate and Transport



Buoyancy: Nanomaterials in Suspension

- The smaller the particle, the more likely to remain in suspension.
- The lighter the particle, the more stable the suspension.
- Dynamic: not at equilibrium.

Particle diameter	Settling rate in water (v_x)	Settling rate in air (v_x)
	cm/hr	
1 mm	$7x10^{2}$	$3x10^{4}$
1 µm	$7x10^{-4}$	$3x10^{-2}$
100 nm	$7x10^{-6}$	$3x10^{-4}$
10 nm	$7x10^{-8}$	$3x10^{-6}$

ARCADIS

Agglomeration

Agglomerate: group of particles held together by relatively weak forces, such as van der Waals force, that can be broken apart. (ASTM International, 2006. E2456-06)

van der Waals force: relatively weak attractive force resulting from transient shifts in electron density.

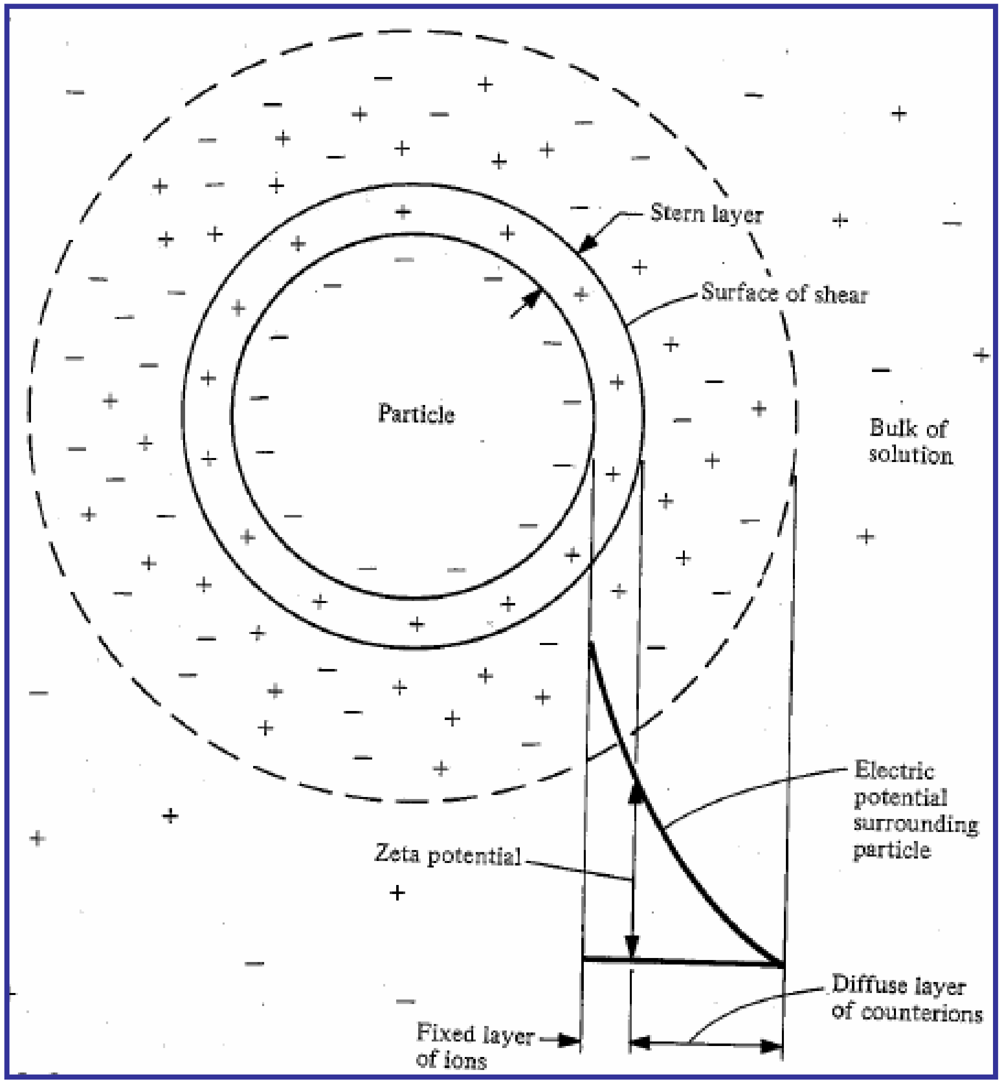
- Hamaker constant represents net van der Waals attraction

Electrostatic repulsion of charged particles counters van der Waals force.

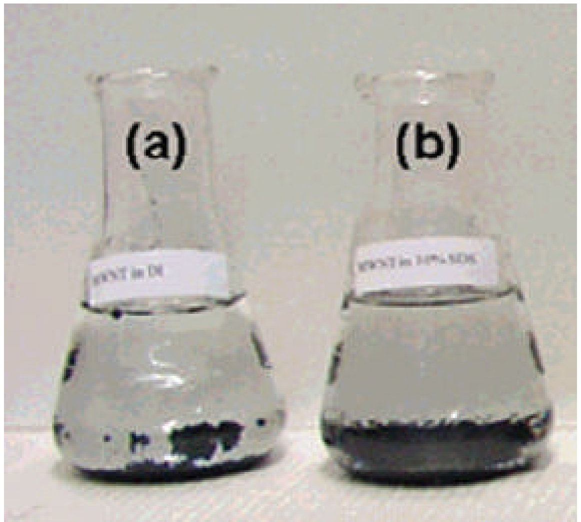
- Particles characterized by surface charge, represented by zeta potential

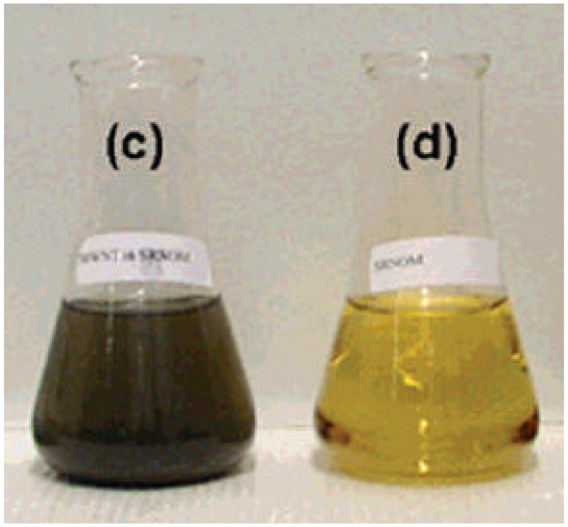
Colloid Theory: Electric Double Layer and Effect of Ionic Strength

- Electrical double layer at every interface between a solid and water
- Counter-ions accumulate in water near surface of particle
- High ionic strength of solution compresses double layer ? limits repulsion, favors agglomeration
- Excess ionic strength can restabilize colloid by charge reversal



Nanomaterials in the environment: Effect of NOM





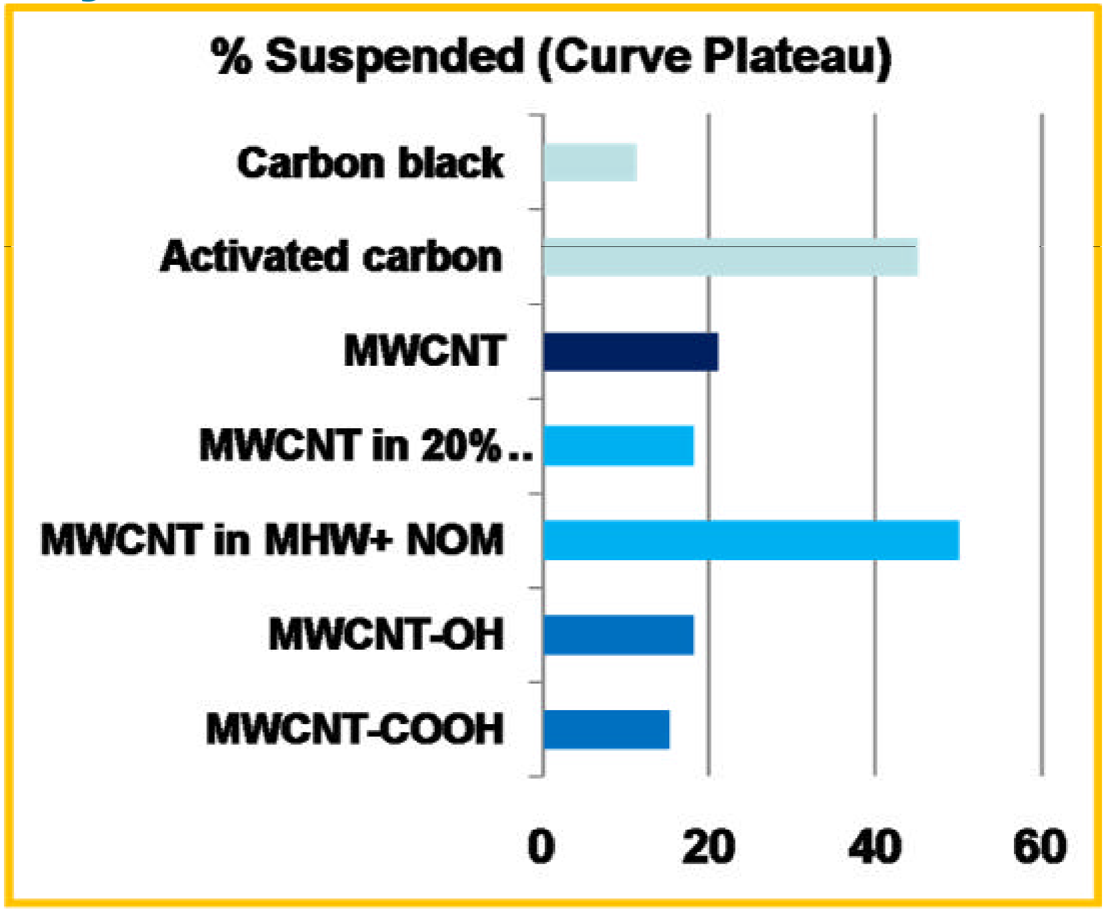
(a) MWCNT in H_2O
(b) MWCNT in 1% SDS

(c,d) Suwannee River with/without MWCNT

Hoon Hyung et al. 2006. Natural Organic Matter Stabilizes Carbon Nanotubes in the Aqueous Phase Environ. Sci. Technol. 41:179 -184.

ARCADIS

Nanomaterials in the Environment: Effect of NOM, salinity, functionalization



adapted from Kennedy et al., 2008.

ARCADIS

Fate and transport of nanomaterials vs. conventional materials

Consideration	Characteristic of Nanomaterial	Parameter	Relevant Characteristic of the Environment
Fixed vs. free	Embedded in matrix vs. particulate		
Buoyancy	Particle size		
	Density		
Reactivity	Surface area		Presence of reactants
	Functionalization		
	Steric hindrance (or lack thereof)	Particle size/shape	
Agglomeration (particle size)	van der Waals forces	Hamaker constant	Natural organic matter
	Electrostatic charge	Zeta potential	pH; ionic strength
Sorption (e.g., to soils)	Can be affected by Brownian motion; sorption to other nanos	Particle size, functionalization	Grain size, charge, organic matter

POTENTIAL RISKS

Cautions in assessing exposure and risk

- Chemical, physical, and biological properties of nanoparticles can differ from those of fine particles or dissolved species of similar chemical composition: existing paradigms may not apply.
- Dosimetry not yet standardized; test methods under scrutiny.
- Consider exposure, not just possible effects.
- Ability to monitor can be limited.
- **Data are preliminary.**
- **Consider experimental design.**
- Beware of generalizations *… even those in this presentation.*

ARCADIS

Principal determinants of nanoparticle toxicity

1. Total surface area presented to the target organ
2. Chemical reactivity of surface
3. Ability to take part in reactions that release free radicals
4. Physical dimensions of particle that allow it to penetrate organ/cells or prevent removal
5. Solubility and/or dissolution

ARCADIS

Routes of Exposure and Potential Human Health Effects

Inhalation

- Lung appears to be most vulnerable target organ
- Small size of nanoparticles can allow for penetration deep into the lung
- Deposit to greater extent than larger respirable particles
- Potential inflammatory toxicology

Ingestion

- Diffusion transport and steric hindrance
- Potential oxidative toxicity

Dermal contact

- Limited exposure from penetration
- Potential phototoxicity, immunotoxicity

Toxicokinetics

- Understanding still very preliminary

- Intravenous administration of nAu to rats:
  - Particles distributed to multiple organs (liver, spleen, heart, brain)
  - Some data show transfer to placenta, foetus
  - Distribution depended on particle size, particle coating, charge

- Intravenous administration of nTiO2 to rats:
  - Highest levels in liver, followed by spleen, lung
  - Highest concentration on day 1 in all organs, decreased at day 14, 28; greatest retention in liver

- Summary: main target organs are spleen and liver (SCENIHR, 2009); further study needed

Ingestion

Exposure scenarios (except for food/medicine): incidental ingestion; accompanies inhalation when cleared from throat/lungs via mucociliary escalator

Moderate to low potential for absorption

- High steric hindrance to diffusion
- Potential for endocytosis (< 300 nm) and systemic distribution

Systemic distribution

- Oral administration of nAu to mice showed higher uptake with smaller size; 4 nm particles found in kidney, liver, spleen, lungs, brain
- Oral administration of nAg to rats (28d) showed dose-dependent accumulation of Ag, particularly in stomach, kidney, liver, lungs, testes, brain, blood.

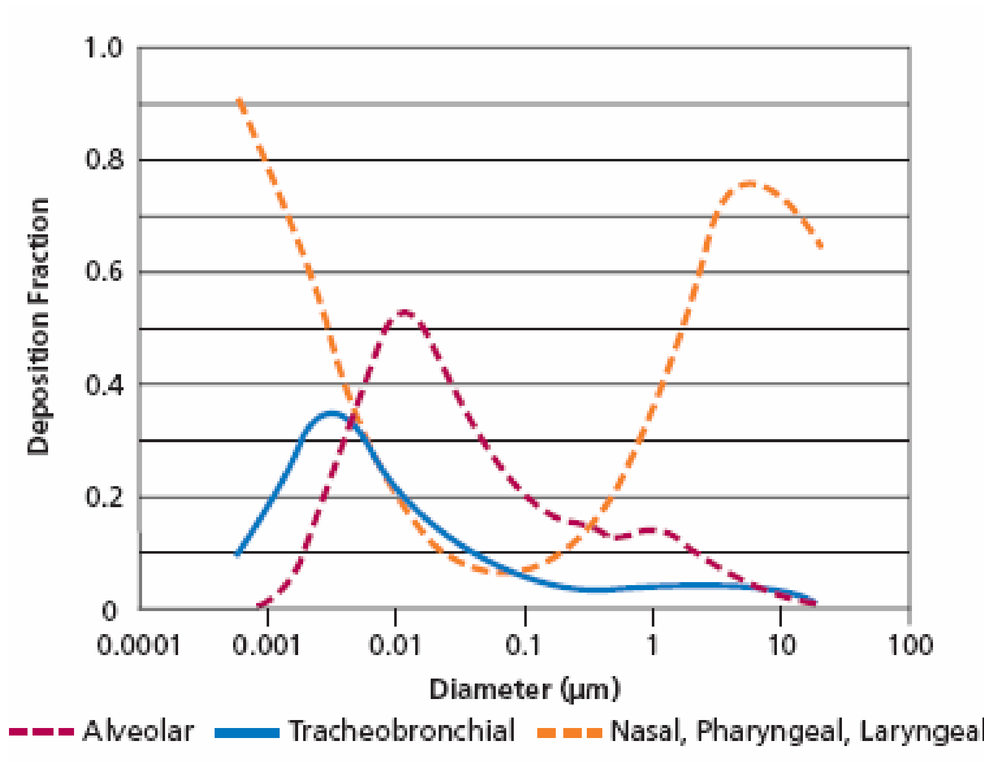
Very limited data on effects

Inhalation of nanoparticles

- "Large and intermediate" size particles trapped in nose or removed from airway by mucociliary escalator.

- Nanoparticles deposited in alveoli; can be removed by scavenger cells.

- Particles 0.1 – 1 nm exhaled.



Oberdorster, et al., 2004.

 25 June 2009

Response to Inhalation: Nanotoxicity

Oxidative stress at molecular/cellular level

Inflammation

- General paradigm for particulates: persistent inflammation leads to fibrosis/cancer
- Animal studies show some nanoparticles induce inflammation, granuloma formation, fibrosis
- Preliminary evidence of possible genotoxicity under some conditions
- No definitive evidence of carcinogenicity

Particle surface area is better dose metric than mass.

ARCADIS

Response to Inhalation: Extrapulmonary translocation

Multiple studies show translocation, including

- In rats, iron particles (35-37nm) deposited in nasal region translocate along olfactory nerve and enter brain (NIOSH, 2007)
- Other studies in lab animals indicate transport of insoluble nanoparticles (20-500 nm) via sensory nerves (olfactory, trigeminus) (NIOSH, 2007)

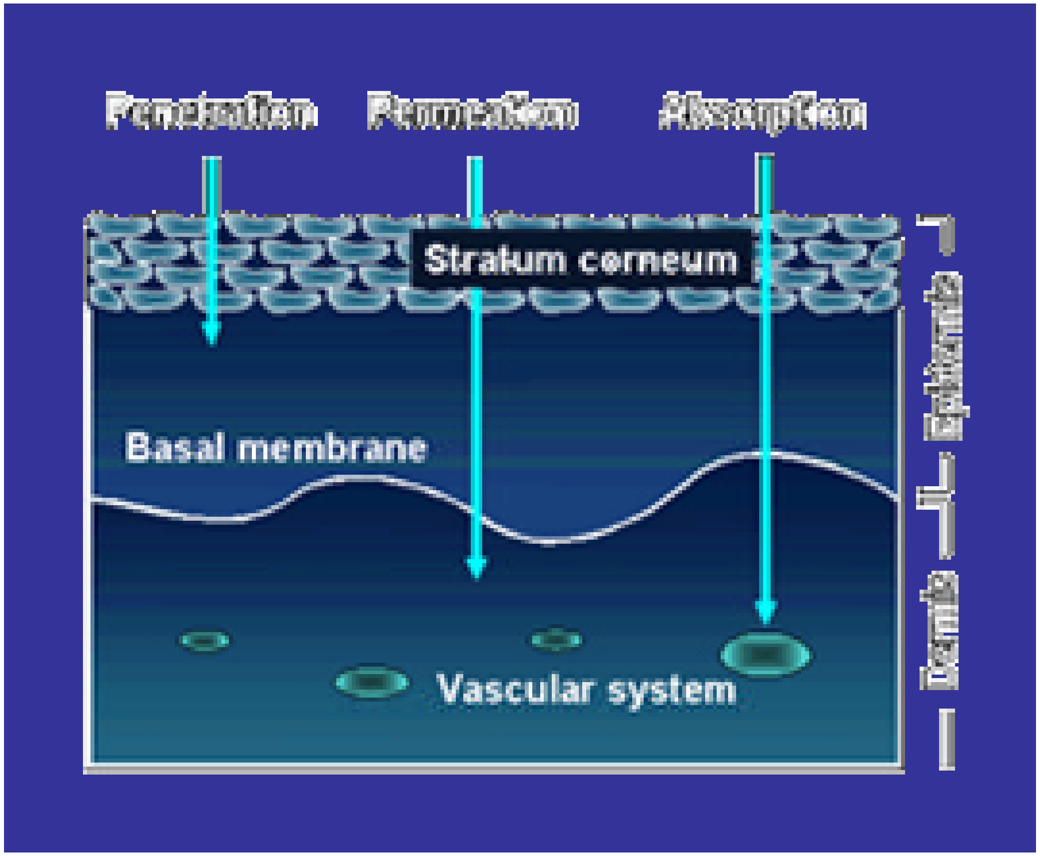
Generally, only a small fraction of the inhaled dose (< 1%)

Not shown in humans

Dermal Absorption

Exposure scenarios: cosmetics/ sunscreen, textiles/ wound dressings, worker exposure, incidental contact

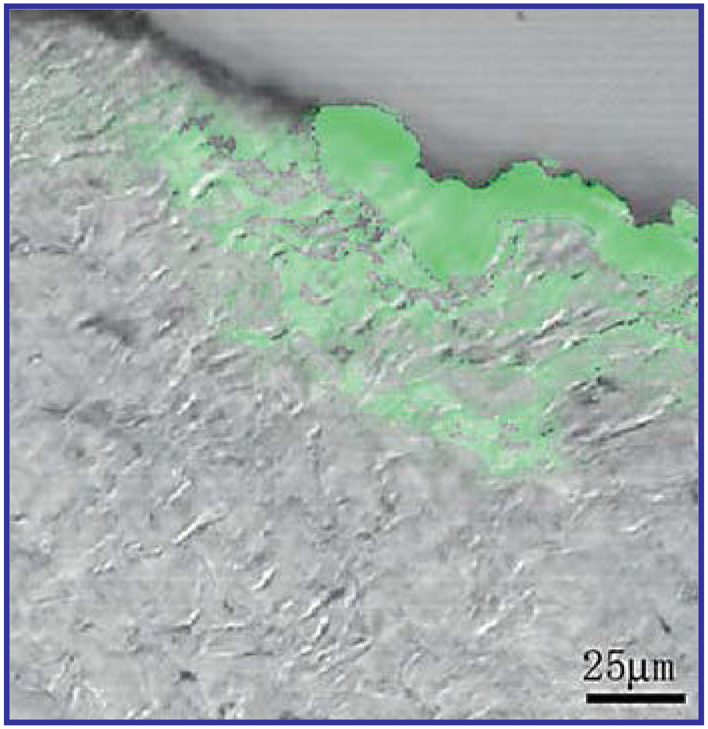
- Transport via permeation or through hair follicles?
- Body's natural defenses may limit penetration
- Depends on dose, size, functionality; site of exposure, skin condition, pH, thickness of stratum corneum
- Concern increases with skin damage; penetration may increase with skin flexing
- Particles reaching dermis can potentially be transported to the lymphatic system



Dermal Absorption: Skin penetration?

Work with quantum dots (QDs):

- QDs applied to porcine skin *ex vivo* penetrated to epidermis/dermis (Ryman-Rasmussen et al., 2006); but subsequent study showed minimal penetration (Zhang et al., 2008).
- Exposure to UV light loosened tight-junction proteins and allowed QDs to pass through skin of mice *in vivo* but "under no circumstances is there evidence for massive QD penetration… QD preferentially collect in folds and defects in the stratum corneum… as well as in hair follicles" (Mortensen et al., 2008).
- QDs applied to rat skin *ex vivo* did not penetrate flexed or tape-stripped skin, but penetrated abraded skin (Zhang et al., 2008).



Quantum dot penetration – abraded rat skin

Zhang et al., 2008

Conclusion: minimal penetration of intact skin; some uncertainty w.r.t. particles < 10nm.

ARCADIS

Dermal Absorption (cont'd) Possible effects

Particle chemistry suggest possibilities:

- Potential for immunotoxicity from some materials.

- Potential for phototoxicity through free radical generation (e.g., C60, TiO_2).

Lessons Learned about Communicating Potential Nanotechnology Risks

- Double-check original sources of popular stories
- Use appropriate qualifiers
- Verify whether reported exposures were actually to nanoparticles, rather than micrometer sized particles, or agglomerates of nanoparticles
- Be cautious about generalizing results from one study to another
- Ask whether or not experimental results can be extended to actual biological systems or the environment
- Probe other possible reasons for toxicity
- Don't assume common-sense macroscopic physics holds at the nanoscale

» Bell, T.E., 2006.

Risk Assessment Conclusions

Environmental fate and transport

- Nanomaterials are not indivisible nor inert; not at equilibrium

  Behavior is size-specific

Exposure and absorption

- Presentation of unique types of materials
- Behavior is size-specific; also depends on other characteristics
- New considerations for diffusion (hindered) and endocytosis
- Pharmacokinetics still up in the air

Toxicity

- Some evidence of oxidative stress and inflammation (lung)
- Data are preliminary, often *in vitro*

Case Study:

NANO SILVER AND WASTEWATER TREATMENT

Case study: nano silver

Illustrates:

- Uncertainty in evaluating proprietary technology.
- Mass balance approach to evaluating exposure potential.
- Application of common sense and available science to headlines.

> *A recent study has found that consumer products that contain silver nanoparticles may be destroying good bacteria used for wastewater treatment"*
>
> **KMWU radio, May 2008**

Regulatory Protections in the U.S. Clean Water Act

- CWA Section 301 -- Requires EPA to set technology-based effluent limitation for point sources
- CWA Section 307 -- Requires EPA to set pretreatment effluent standards
- CWA Section 302 -- Authorizes EPA to set water quality-related effluent limitations if EPA determines Section 301 standards (water quality standards for waters of the U.S.) are insufficient

Regulatory Developments in the U.S.: FIFRA

- Requires pesticide registration (after demonstration that it will not pose an unreasonable risk)
- Antimicrobial products can be regulated as pesticides
- In the news:
  - Samsung washing machine
  - IOGEAR computer peripherals

Press release 03/05/2008 :

U.S. EPA fines Southern California technology company $208,000 for "nano coating" pesticide claims on computer peripherals

This is an example of an unregistered product that asserts unsubstantiated antimicrobial properties.

http://yosemite.epa.gov/opa/admpress.nsf/2dd7f669225439b7852573590400c31/16a190492f2f25d85257403005c2851!OpenDocument

Sources: consumer products containing nano silver

http://www.nanotechproject.org/inventories/consumer/search/page13/?search=1&keywords=silver, 22 June 09

Samsung SilverCare^{TM} Washing Machine

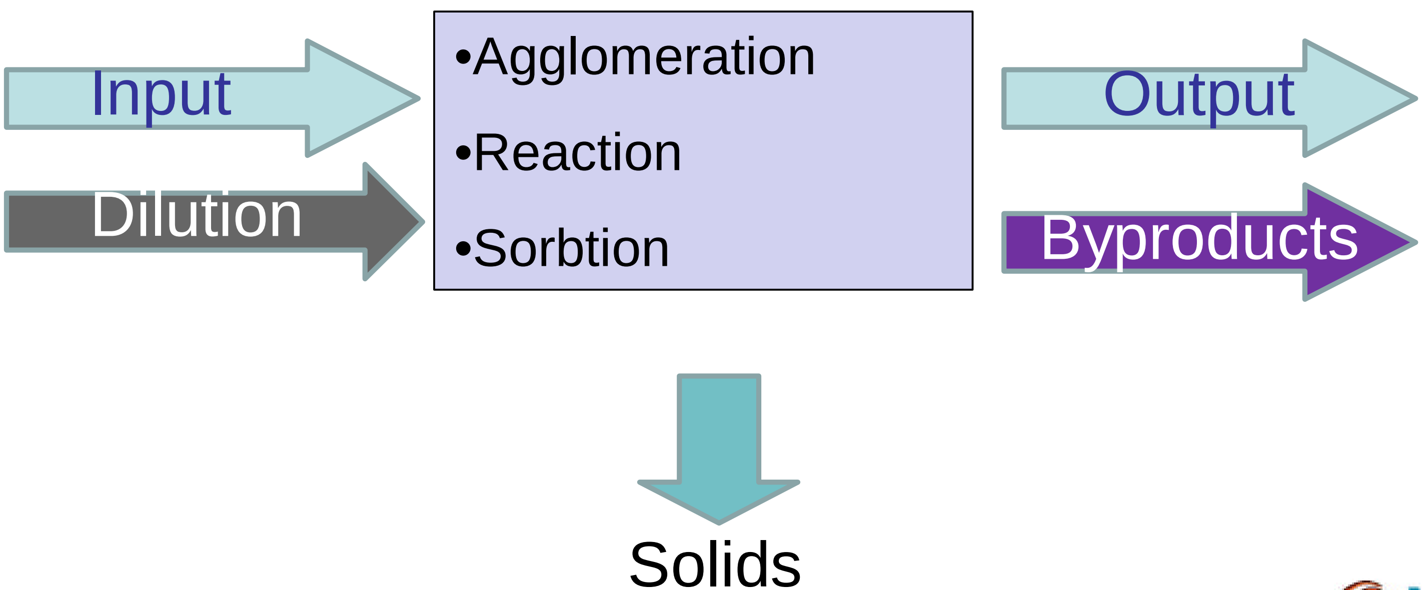
- Samsung stated that silver “eradicate[s] bacteria and mold from inside the washer” and “stick[s] to the fabric” to provide anti-bacterial function for up to 30 days.
- Reportedly $10M invested in development.
- Proprietary technology.

> [The German branch of Friends of the Earth] criticized that considerable amounts of silver could enter sewage plants and seriously trouble the biologic purification process of the waste water. In addition, silver nanoparticles were blamed to have a toxic effect on different kinds of cells.
>
> \- As cited at www.foresight.org

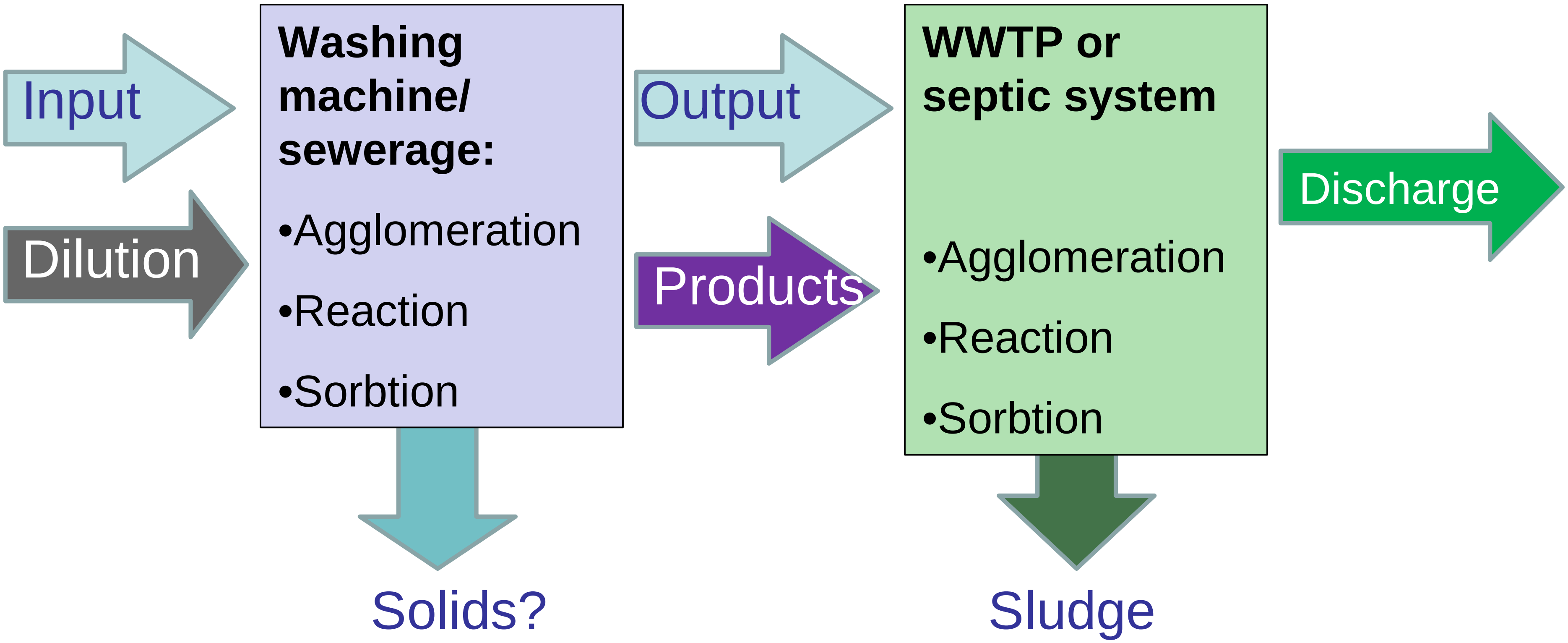
How much silver could be released?

Mass balance:

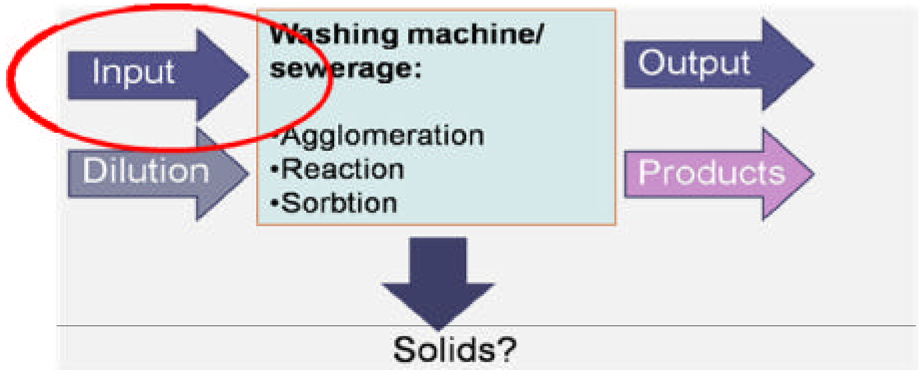
- Generation
- Removal / sorbtion
- Dilution



Two-step calculation



Generation (input)

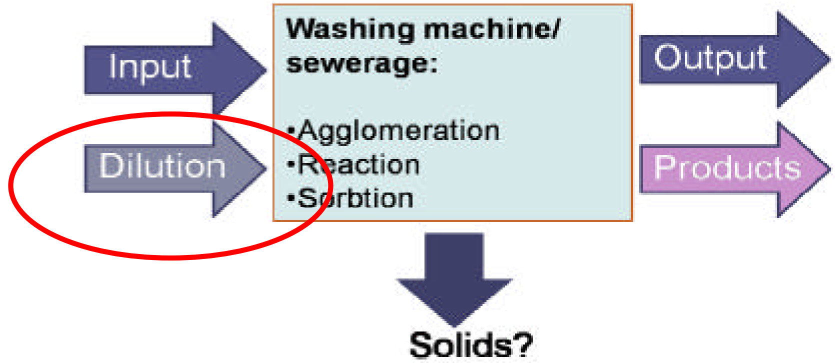


Samsung literature described in different ways: (www.samsung.com)

- 400 billion silver ions generated during each wash cycle; OR
- "Electro currents nano-shave two silver plates the size of large chewing gum sticks", which reportedly last for 3,000 wash cycles; OR
- Use of washing machine releases 0.05 grams per year.

Nano silver particles or ionic silver?

Dilution



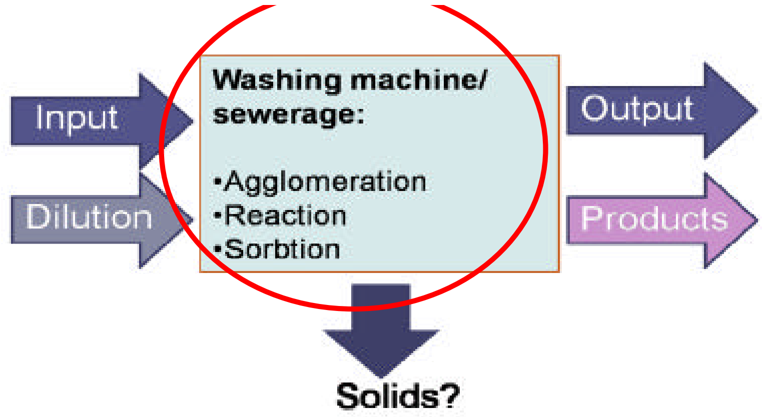
Estimates:

- Wash cycle uses 12.68 gal water
- Typical residence generates 70 gallons wastewater per person per day

Unknowns:

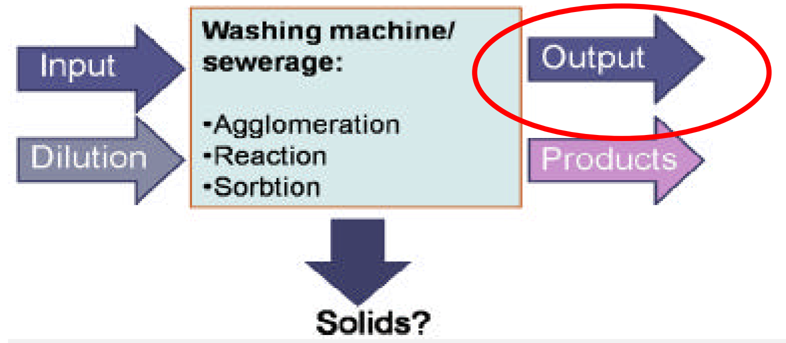
- Number of SilverCare™ washing machines in community?
- Number of people in community?
- Amount of laundry per person per day?
- Other sources of non-domestic wastewater in community?

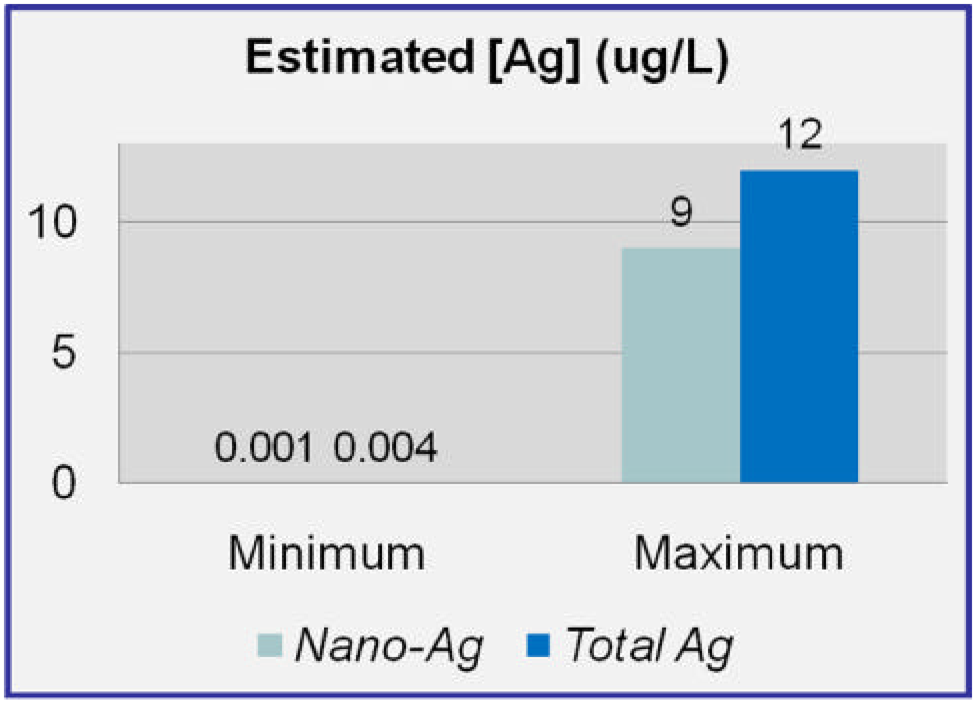
Removal / sorption



- Samsung: silver "sticks to the fabric"
- Sorption to other solids?
- Agglomeration?
- Chemical/ biological reactions?

Results of *Preliminary* mass balance: Ag entering WWTP





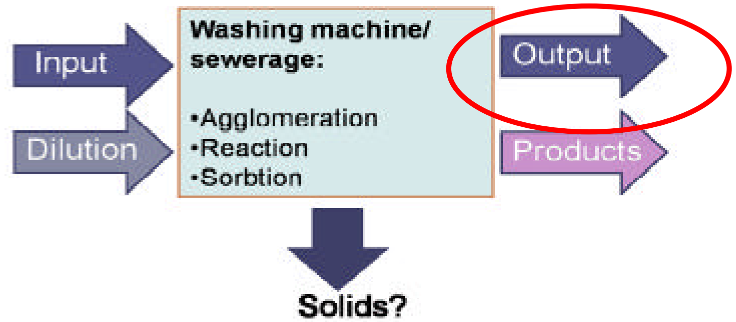
Nanotechnology and the Environment, 2008;

U.S. Environmental Protection Agency. Current National Recommended Water Quality Criteria. http://earth1.epa.gov/waterscience/criteria/wqcriteria.html

- Range of assumptions generates range of estimates.
- Maximum estimate is <u>extreme</u> <u>upper</u> <u>bound</u>.
- Minimum does not reflect all dilution (conservative).

- Ag measured in discharge from washer at ~ 10 ug/L (Farkas et al., 2009).

Other sources from consumer products?



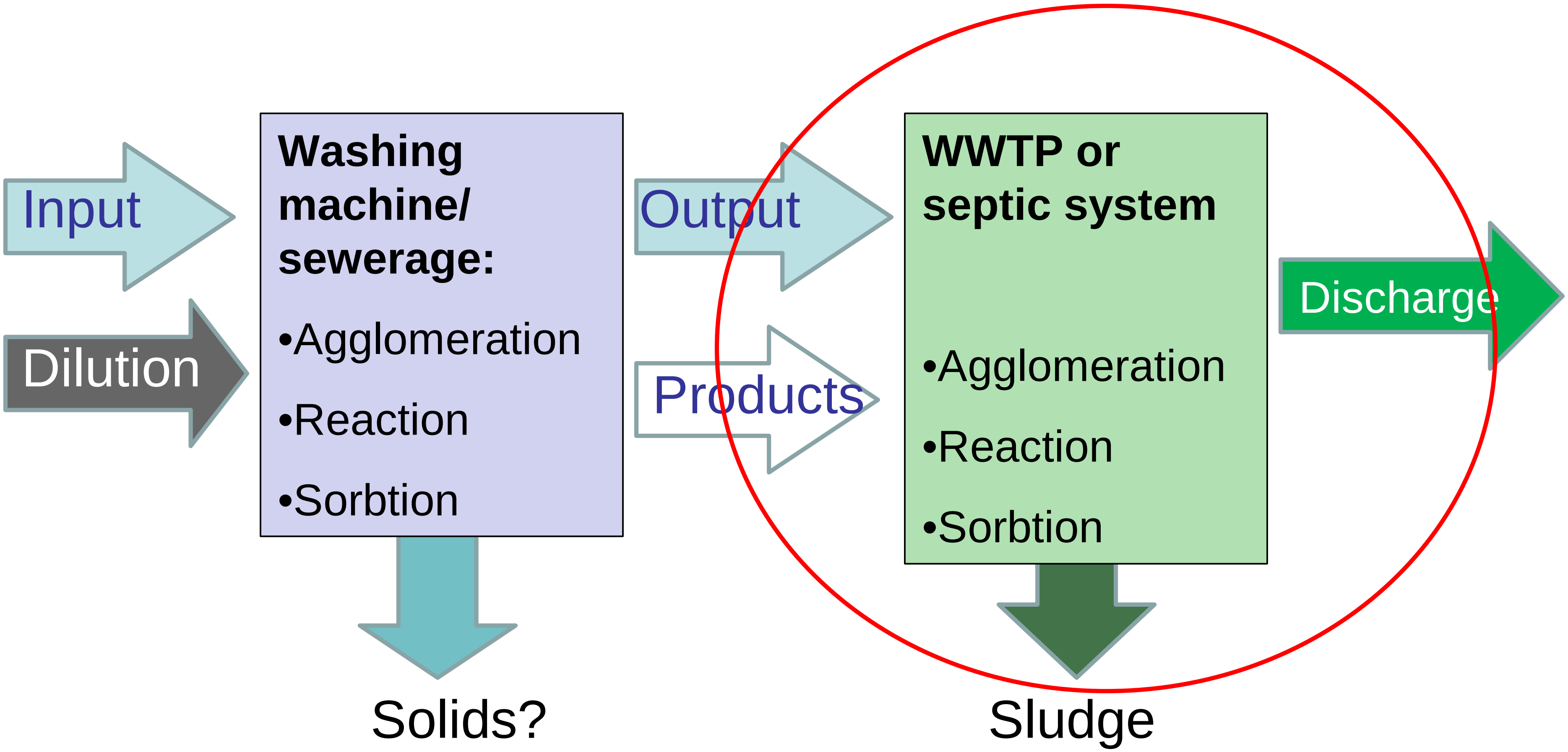
Experiments simulated washing nano Ag socks (Benn and Westerhoff, 2008)

- Not all socks actually contained Ag
- [Ag] = 60-500 µg/L under simulated wash conditions
- Likely overestimate by factor of more than 25 based on experimental design

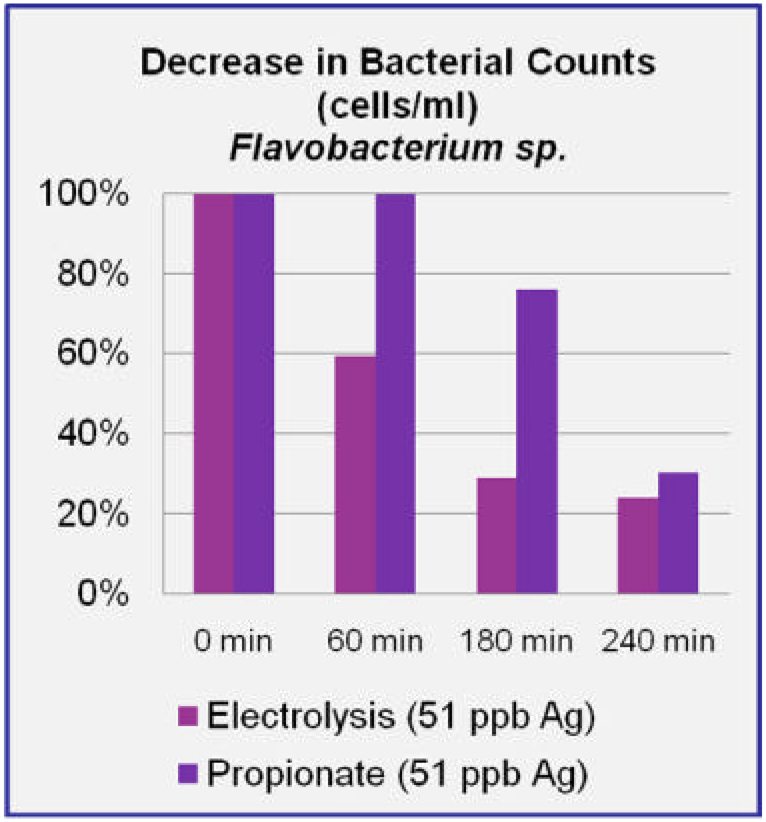
From left to right: 1) Lounge (Sharper Image), 2) Athletic (Sharper Image), 3) XStatic (Fox River). 4) E47 (Arctic Shield). 5) Zensah

Photo from: "Nanoparticle Interactions during wastewater and water treatment". Nanotechnology – Applications and Implications for Superfund: Session 6: "Nanotechnology – Fate and Transport of Engineered Nanomaterials"

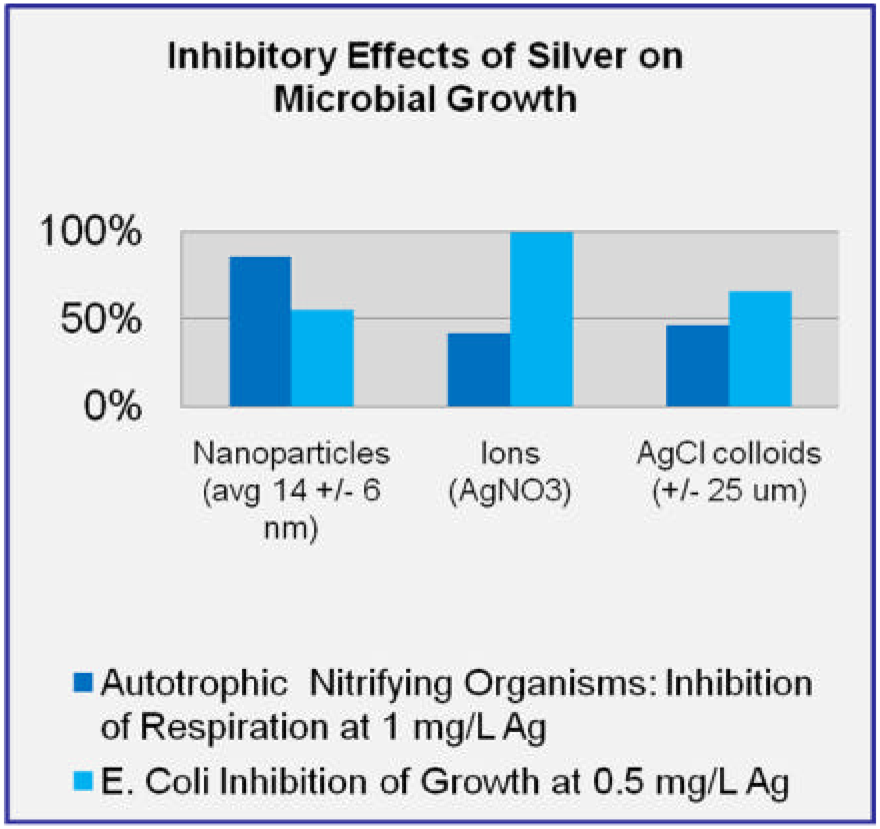
Next step: nano Ag enters wastewater treatment plant or septic system



Could concentrations in WWTP be of concern? *Microbial data*

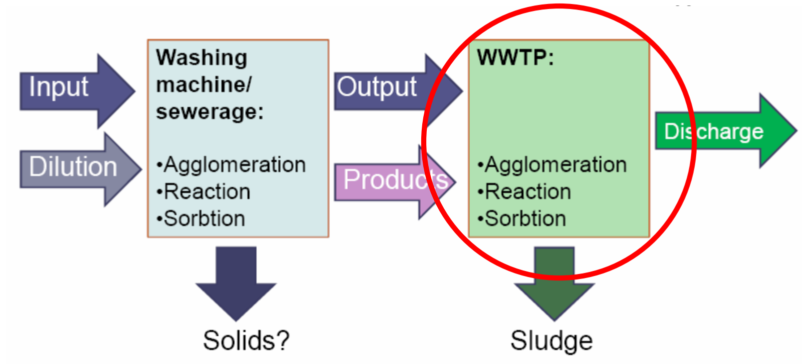


Cliver et al., 1970



Choi et al., 2008.

Treatment of Ag in WWTP



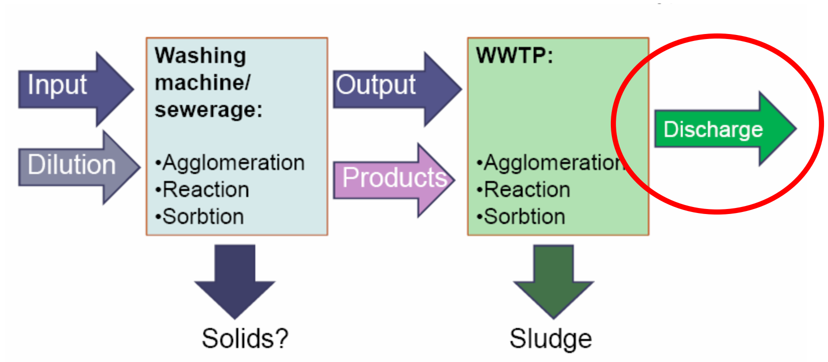
Batch adsorption (isotherm) experiments to quantify removal. (Benn and Westerhoff, 2008)

- Biomass/activated sludge from WWTP
- Two solutions: wash water from nano-Ag socks, Ag^{+}; initial [Ag] = 60-500 µg/L

Results of model simulations based on Freundlich isotherm:

- Influent 5 µg/L ✍ effluent 0.001 µg/L, biosolids 2.8 mg- Ag/kg
- Treated effluent would not exceed 100 µg/L (SMCL) until influent concentration reached 2.1 mg/L, or AWQC until influent reached 0.36 mg/L.

Estimated Releases to the Environment



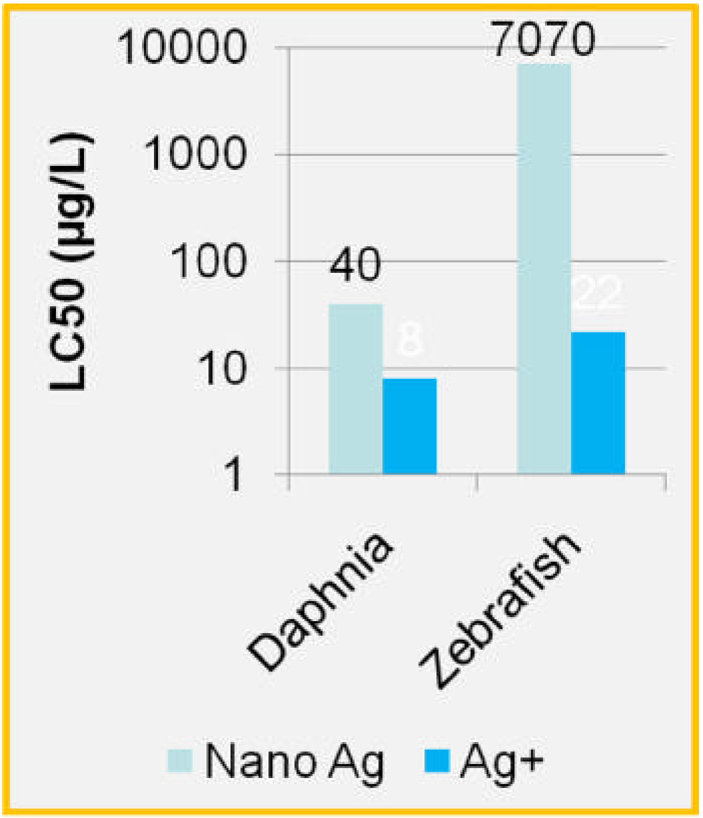
Exposure Point	**Conc., 1st approx. (µg/L)**	**Ref.**
Entering WWTP (WM)	0.001 – 10	Sellers et al., 2008
WWTP effluent, for influent 5 µg/L	0.001	Benn and Westerhoff, 2008
Surface water (WM, S, SP)	29 – 189	Luoma, 2008
Surface water	40 – 340	Blaser et al., 2007
Surface water, all sources	0.03 – 0.08	Mueller and Nowak, 2008

Sources: WM = washing machine; S = socks; SP = swimming pools

How well do we understand the environmental effects of nanomaterials?

- Preliminary understanding: most research done in last 2-3 years
- Testing challenges
- Concerns, depending on the nanomaterial studied:
  - Certain nanomaterials are antimicrobial due to membrane damage, production of ROS, oxidation/damage to proteins, interference with e^- transport/respiration, potential DNA damage
  - Testing on higher aquatic forms shows potential for effects on behaviour, reproduction, growth and development, ROS production, induction of inflammatory response, and cytotoxic effects. Some evidence of potential transfer to embryos, accumulation, and potential food chain transfer.

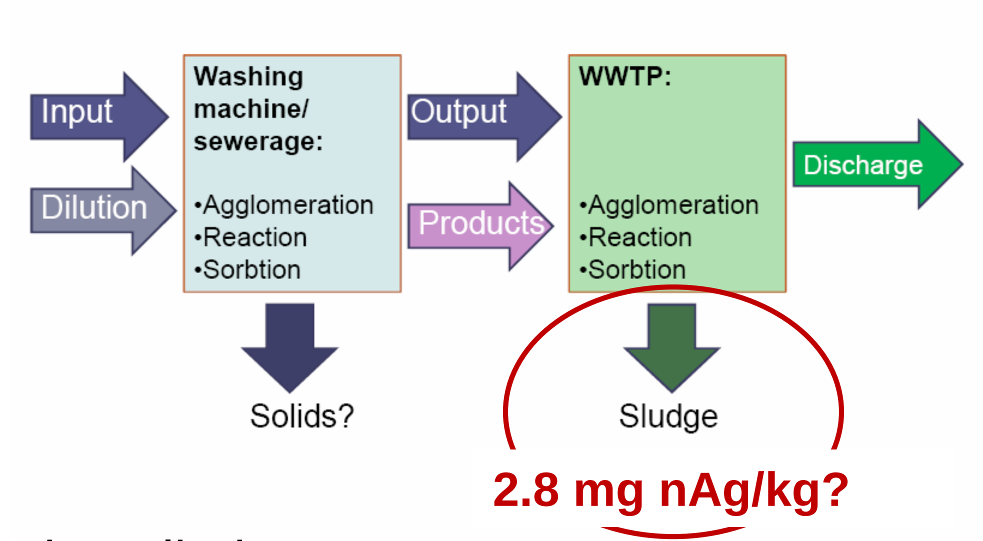
Could Concentrations of nAg Released to Environment Be of Concern? *Bioassay Data*



(Griffitt et al., 2008)

- Zebrafish embryos:
  - Development normal at 0.008 µg/L; beyond 0.019 µg/L 11 nm Ag, produced dead or deformed zebrafish (Lee et al., 2008)
  - 1-5,000 µg/L showed no effect on development or survival, but some effect on gene expression at highest levels (Rojo et al., 2007)
  - 5-100 **m**g/L nanoparticles capped with BSA or starch showed accumulation in brains, phenotypic defects, altered physiologic function. Dose-dependent toxicity hindered normal development (Valiyaveettil, 2008)

What about nAg in sludge?



Fate of sludge:

Landfilled? Incinerated? Land-applied?

Ecotoxicity to soil nematode (Roh et al., 2009):

- Exposed to 0.05, 0.1 and 0.5 mg/L nAg (sonicated), 14-20 nm particles
- Effects (nAg > $AgNO_3$):
  - Decreased reproduction
  - Concurrent gene modification
  - Possible oxidative stress

Was the headline right?

- Potential for nano Ag to enter the environment depends on consumer choices, amount of nano Ag in consumer products, and physical processes (dilution, reaction, sorption). *None of those factors are currently well quantified.*

- Estimates of concentrations released into aquatic environment vary over five orders of magnitude.

- Gross effects in aquatic environment unlikely based on current data. *Potential for subtle effects?*

ARCADIS

SUMMARY AND CONCLUSIONS

Summary and Conclusions: Uses of Nanomaterials

Nanomaterials are used in ~ 800 commercial products and new medical applications because:

- At this particle size, different laws of physics may predominate, changing a material's properties, and
- Increased relative surface area per unit mass increases chemical reactivity, making many nanoparticles useful catalysts.

Some of these applications offer environmental benefits, including:

- Energy savings
- Alternative energy supplies
- Efficient use of raw materials
- Environmental remediation and detection
- Medical applications

Summary and Conclusions: Fate and Transport

Nanoparticles in metastable suspension

- Small sized particles stay in suspension
- Agglomeration increases particle size ✍ particles drop out of suspension

Influenced by

- Steric hindrance
- Other constituents

Can’t assume equilibrium

Summary and Conclusions: Potential Risks

- *In vitro* tests of certain nanomaterials have shown effects on mammalian cell lines.
- Some laboratory bioassays have demonstrated toxic effects.
- Hazards may result from the inhalation of nanoparticulates, which can cause inflammation or oxidative-stress response.
- Consider the context:
  - Dosing methods may overestimate reflect real-world conditions.
  - Measures taken to prepare test solutions may introduce other toxicants or otherwise represent artificial conditions.
  - Other materials used the manufacturing process or part of the final product may present hazards.

Recommendations

- Monitor regulatory and technical developments
- Interpret literature reports of experimental results carefully
- Expect the unexpected
- Consider Life Cycle thinking

Are the rewards worth the risks?

"Learn from yesterday, live for today, hope for tomorrow. The important thing is not to stop questioning."

- *Albert Einstein*

For more information…

International Council on Nanotechnology
http://icon.rice.edu/

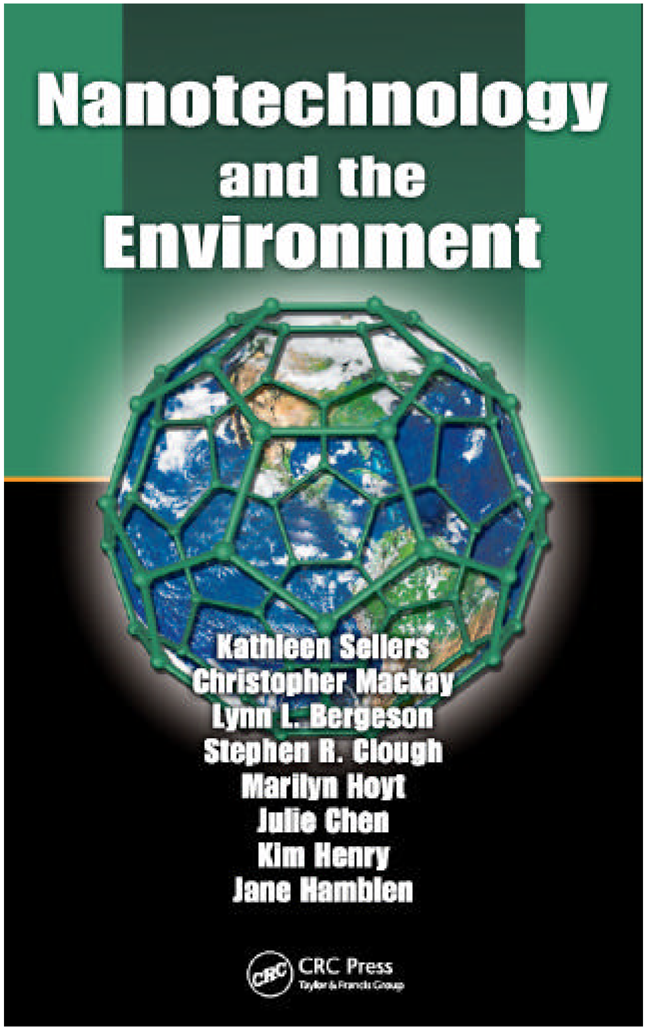
Project on Emerging Nanotechnologies, Woodrow Wilson Institute www.nanotechproject.org/

U.S. EPA Nanoscale Materials Stewardship Program
www.epa.gov/oppt/nano

NIOSH Nanoparticle Information Library
http://www2a.cdc.gov/niosh-nil/index.asp

OECD http://www.oecd.org/env/nanosafety Database on Research into Safety of Manufactured Nanomaterials:
http://www.oecd.org/document/26/0,3343,en_2649_37015404_42464730_1_1_1_1,00.html

Nanotechnology Law Blog
http://nanotech.lawbc.com/articles/environmental-issues/



References

- American Cancer Society, 2007. Skin Cancer Facts. Available at www.cancer.org.
- ASTM International. 2006. Designation: E 2456 – 06. Standard Terminology Relating to Nanotechnology.
- Barker and Branch, 2008. The interaction of modern sunscreen formulations with surface coatings. Progress in Organic Coatings. 62:313-320.
- Bell, T.E., 2006. Reporting Risk Assessment of Nanotechnology: A reporter's guide to sources and research issues http://www.nano.gov/html/news/reporting_risk_assessment_of_nanotechnology.pdf
- Benn, T.M. and Westerhoff, P., 2008. Nanoparticle siver released into water from commercially available sock fabrics. Environ Sci Technol 42: 4133-4139.
- Bigorgne, E., et al., 2009. Ecotoxicological effect of alterated TiO2 nanocomposite on the earthworm, *Eisenia fetida*. Poster preseted at SETAC Europe: 19th Annual Meeting. 31 May – 4 June 2009, Goteborg, Sweden.

References, cont'd

Braydich-Stolle, L., et al. 2005. In Vitro Cytotocicity of Nanoparticles in Mammalian Germline Stem Cells. *Toxicological Sciences* 88, no.2:412-419.

Brunner, T. J., P. Wick, P. Manser, et al. 2006. In Vitro Cytotoxicity of Oxide Nanoparticles: Comparison to Asbestos, Silica, and the Effect of Particle Solubility. *Environ. Sci. Technol.* 40:4374-4381.

Calafat, A.M., et al., 2008. Concentrations of the Sunscreen Agent Benzophenone-3 in Residents of the United States: National Health and Nutrition Examination Survey 2003-2004. Environmental Health Perspectives. 116(7): 893-897.

Choi. O., *et al*., 2008. The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth. *Water Res*. Doi:10.1016/j.watres.2008.02.021.

Choi, J-Y., et al., 2009. The Impact of Toxicity Testing Costs on Nanomaterial Regulation. Environ. Sci. Technol., 43(9): 3030-3034.

Cliver, D. O., et al., 1970. Biocidal Effects of Silver, Final Technical Report. Prepared for: National Aeronautics and Space Administration. NASA CR 108338.

Environmental Defense and DuPont. 2007. Nano Risk Framework. 21 June. www.NanoRiskFramework.com .

References, cont'd

Environmental Defense and DuPont. 2007. Nanomaterial Risk Assessment Worksheet: Zero Valent Nano Sized Iron Nanoparticles (nZVI) for Environmental Remediation. http://www.environmentaldefense.org/documents/6554_nZVI_Summary.pdf

Environmental Defense and DuPont. 2007. Nanomaterial Risk Assessment Worksheet: Incorporation of Single and Multi Walled Carbon Nano Tubes (CNTs) into Polymer Nanocomposites by Melt Processing. http://www.environmentaldefense.org/documents/6553_CNTs_Summary.pdf.

Environmental Working Group. Sunscreens: About Active Ingredients. http://www.cosmeticsdatabase.com/special/sunscreens2008/report_active.php?nothanks=1

European Commission, 2005. Social values, Science and Technology. Special Eurobarometer 225/Wave 63.1 – TNS Opinion & Social. http://ec.europa.eu/public_opinion/archives/ebs/ebs_225_report_en.pdf

European Commission, 2005. Europeans, Science and Technology. Special Eurobarometer 224/Wave 63.1 – TNS Opinion & Social. http://ec.europa.eu/public_opinion/archives/ebs/ebs_224_report_en.pdf

Farkas, J., et al., 2009. Initial assessment of silver nanoparticles from washing machines. Poster presentation at SETAC Europe 19th Annual Meeting, 31 May-4 June 2009. Goteborg, Sweden.

References, cont'd

Friends of the Earth, 2007. Nanotechnology & Sunscreens: a consumer guide for avoiding nano-sunscreens. Available at http://www.foe.org

Griffitt, R. J., et al., 2008. Effects of particle composition and species on toxicity of metallic nanomaterials in aquatic organisms. Environmental Toxicology and Chemistry. 27(9): 1972-1978.

Gwinn, M. R. and V. Vallyathan, 2006. Nanoparticles: Health Effects – Pros and Cons. Environmental Health Perspectives, 114(12):1818-1825.

Hagens et al., 2007. What do we (need to) know about the kinetic properties of nanoparticles in the body? Regulatory Toxicology and Pharmacology 49: 217-229.

- Hunde-Rinke, K. and M. Simon. 2006. Ecotoxicological effects of photocatalytic active nanoparticles)Ti)2) on algae and daphnids. *ESPR-Environ Sci & Pollut Res* (OnlineFirst):1-8.

Hussain, S. M., et al. 2006. The Interaction of Manganese Nanoparticles with PC-12 Cells Induces Dopamine Depletion. *Toxicological Sciences* 92 (2):456-463.

Hyung, H. et al. 2006. Natural Organic Matter Stabilizes Carbon Nanotubes in the Aqueous Phase Environ. Sci. Technol. 41:179 -184**.**

Johnson, A., et al., 2009. Should we be concerned about the discharge of sunscreen nano TiO2 to the environment? Poster presented at SETAC Europe: 19th Annual Meeting, 31 May-4 June 2009. Goteborg, Sweden.

Kang, S.J., et al., 2008. Titanium Dioxide Nanoparticles Trigger p53-Mediated Damage Response in Peripheral Blood Lymphocytes. Environmental and Molecular Mutagenesis 49:399^405.

References, cont'd

Kennedy, A.J., et al., 2008. Factors influencing the partitioning and toxicity of nanotubes in the aquatic environment. Environmental Toxicology and Chemistry 27(9): 1932-1948.

Klaine, S.J., et al., 2008. Nanomaterials in the Environment: Behavior, Fate, Bioavailability, and Effects. Envtl Toxicology and Chemistry, 27(9): 1825-1851.

Lademann, J. et al., 1999. Penetration of Titanium Dioxide Microparticles in a Sunscreen Formulation into the Horny Layer and the Follicular Orifice. Skin Pharmacol. Appl. Skin Physiol. 12: 247-256.

Lee, C. et al., 2008. Bactericidal Effect of Zero Valent Iron Nanoparticles on Eschericia coli. Environ. Sci. Technol., 42: 4927-4933.

Limbach, L.K., et al., 2007. Exposure of Engineered Nanoparticles to Human Lung Epithelial Cells: Influence of Chemical Composition and Catalytic Activity on Oxidative Stress. Environ. Sci. Technol., published on the web 10.1021/es062629t.

Long, C., et al., 2006. Titanium Dioxide (P25) Produces Reactive Oxygen Species in Immortalized Brain Microglia (BV2): Implications for Nanoparticle Neurotoxicity. Environ. Sci. Technol. 40(14): 4346-4352.

Lovern, S. B. and R. Klaper 2006. "Daphnia magna mortality when exposed to titanium dioxide and fullerene (C60) nanoparticles." *Environ. Toxicol. Chem.* 25(4): 1132-1137.

Maynard, A.D., et al., 2004. Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. J. Toxicol. Environ. Health, 67(1): 87-107.

References, cont'd

McDonald, J., 2007. Pulmonary and Systemic Inhalation Toxicity of Multiwalled Carbon Nanotubes. Proceedings of the Interagency Workshop on the Environmental Implications of Nanotechnology. Sponsored by USEPA, ORD. Sept. 5-7, 2007.

Mortensen, L.J., et al., 2008. In Vivo Skin Penetration of Quantum Dot Nanoparticles in the Murine Model: the Effect of UVR. Nano Letters, 8(9): 2779-2787.

Muller, J., et al., 2008. Clastogenic and aneugenic effects of multi-wall carbon nanotubes in epithelial cells. Carcinogenisis 29(2): 427-433; doi:10.1093/carcin/bgm243.

- Nielsen, G.D., et al., 2008. *In vivo* Biology and Toxicology of Fullerenes and their Derivatives. Basic & Clinical Pharmacology & Toxicology. 103: 197-208.
- NIOSH, 2007. Approaches to Safe Nanotechnology: An Information Exchange with NIOSH. www.cdc.gov/niosh/topics/nantech/safenano/healthconcerns.html
- Nohynek, G.J., et al., 2007. Grey Goo on the Skin? Nanotechnology, Cosmetic and Sunscreen Safety . Critical Reviews in Toxicology. 37:251-277.
- OECD, 2008. Series on the Safety of Manufactured Nanomaterials, Number 6. List of Manufactured Nanomaterials and List of Endpoints for Phase One of the OECD Testing Programme. ENV/JM/MONO(2008)13. June 2008.

Poland, C.A., et a., 2008. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nature Nanotechnology, 3:423-428.

Pont, A.R., et al., 2002. Active Ingredients in Sunscreens Act as Topical Penetration Enhancers for the Herbicide 2,4D. Proceedings of the International Conference on Occupation & Environmental Exposures of Skin to Chemicals: Science & Policy. Hilton Crystal City, September 8-11, 2002. Available at: http://www.cdc.gov/niosh/topics/skin/conference/s2p7.html.

References, cont'd

Peter D. Hart Research Associates, Inc., 2007. Awareness of and Attitudes Toward Nanotechnology and Federal Regulatory Agencies. A Report of Findings Based on a National Survey Among Adults. Conducted on Behalf of: Project on Emerging Nanotechnologies, The Woodrow Wilson International Center for Scholars. September 25, 2007. www.wilsoncenter.org

Roh, J., 2009. Ecotoxicity of Silver Nanoparticles on the Soil Nematode *Caenorhabditis elegans* Using Functional Ecotoxicogenomics. Environ. Sci. Technol., 42(10): 3933-3940.

Ries LAG, et al., (eds). SEER Cancer Statistics Review, 1975-2005, National Cancer Institute. Bethesda, MD, http://seer.cancer.gov/csr/1975_2005/, based on November 2007 SEER data submission, posted to the SEER web site, 2008.

Robichaud, C. O., D. Tanzil, U. Weilenmann, and M. R. Wiesner. 2005. Relative Risk Analysis of Several Manufactured Nanomaterials: an Insurance Industry Context. *Environ. Sci. Technol.* 39 (October):8985-8994

Rojo, I., et al. 2007. Toxicogenomics study of nanomaterials on the model organism Zebrafish. NSTI-Nanotech 2007, www.nsti.org, ISBN 1420061836 (Vol. 2).

Rouse, J. G., J. Yang, J. P. Ryman-Rasmussen, A. R. Barron, and N. A. Monteiro-Riviere. 2007. Effects of Mechanical Flexion on the Penetration of Fullerene Amino Acid-Derivatized Peptide Nanoparticles through Skin. *Nano Lett.* 7:155 -160.

The Royal Academy of Engineering, the Royal Society. 2004. Nanoscience and nanotechnologies: opportunities and uncertainties, Chapter 5. 29 July. http://www.royalsoc.ac.uk.

References, cont'd

Sayes, C.M., et al., 2006. Correlating Nanoscale Titania Structure with Toxicity: A Cytotoxicity and Inflammatory Response Study with Human Dermal Fibroblasts and Human Lung Epithelial Cells. Toxicol. Sci., 92(1): 174-185.

SCENIHR (Scientific Committee on Emerrging and Newly Identified Health Risks), 2007. Opinion on the Appropriateeness of the Risk Assessment Methodology in Accordance with the Technical Guidance Documents for New and Existing Substances for Assessing the Risks of nanomaterials. 21-22 June 2007.

SCENIHR, 2009. Risk assessment of products of nanotechnologies, 19 January 2009. http://ec.europa.eu/health/ph_risk/risk_en.htm

Schulz, J., et al., 2002. Distribution of sunscreens on skin. Advanced Drug Delivery Reviews. 54 Suppl. 1, S157-S163.

Sellers, K., et al., 2008. *Nanotechnology and the Environment*. Taylor & Francis/CRC Press.

Shvedova, A. A., et al. 2005. Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice. *Am. J. Physiol. Lung Cell. Molec. Physiol.* 289:L698-L698.

Scheufele, D.A., et al., 2008. Religious beliefs and public attitudes toward nanotechnology in Europe and the United States. Nature Nanotechnology. Letters. Published on line 7 December 2008.

Shatkin. J. , 2008. Nanotechnology: health and environmental risks. Boca Raton, FL: CRC Press.

Imagine the result

