ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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Occupational, consumer and environmental exposure to nanomaterials

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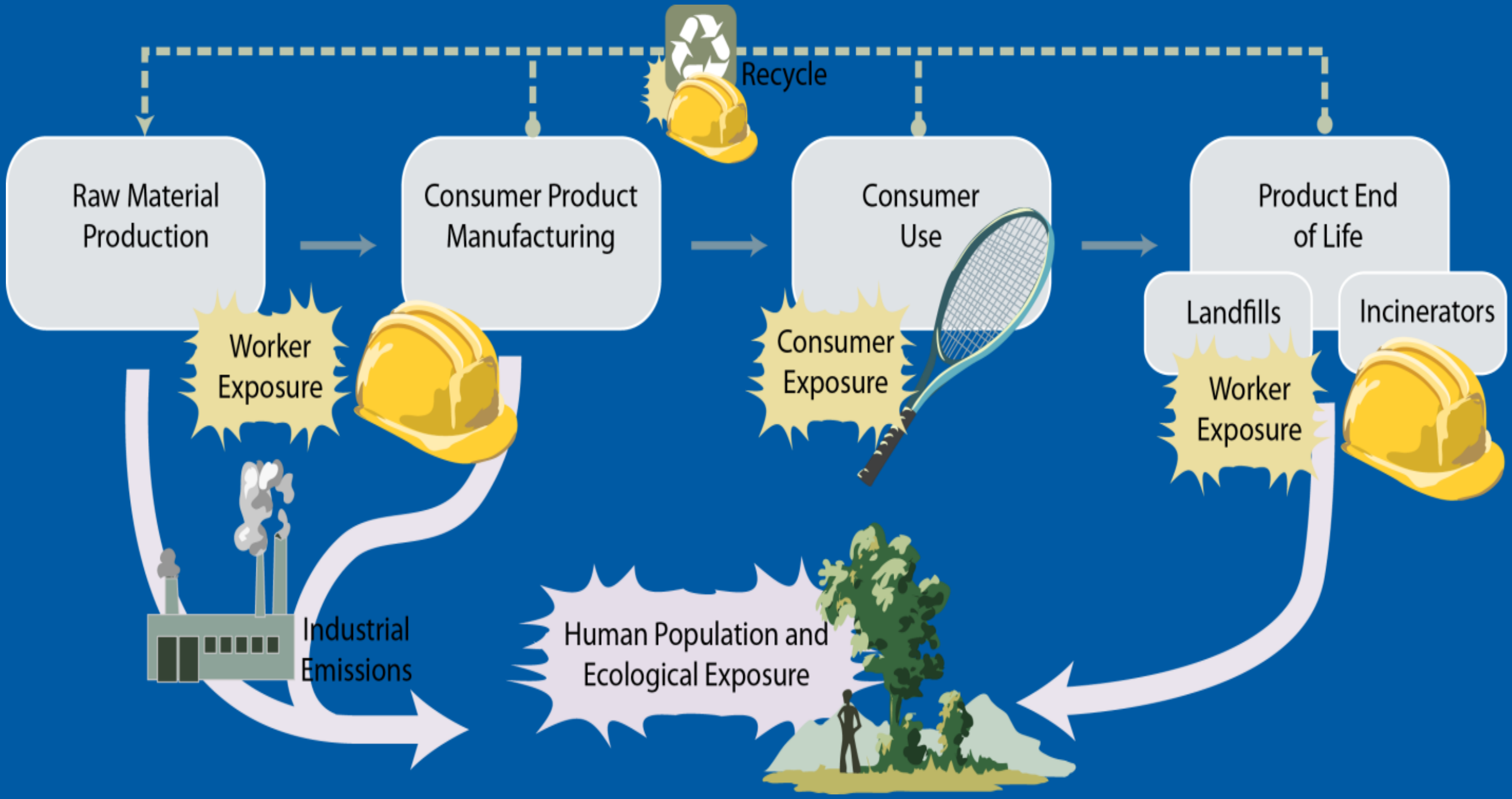
NANOMATERIAL EXPOSURE

Organization for Economic Cooperation and Development

- Working Party on Manufactured Nanomaterials
- Working Party on Resource Productivity and Waste

Nanomaterial Life Cycle



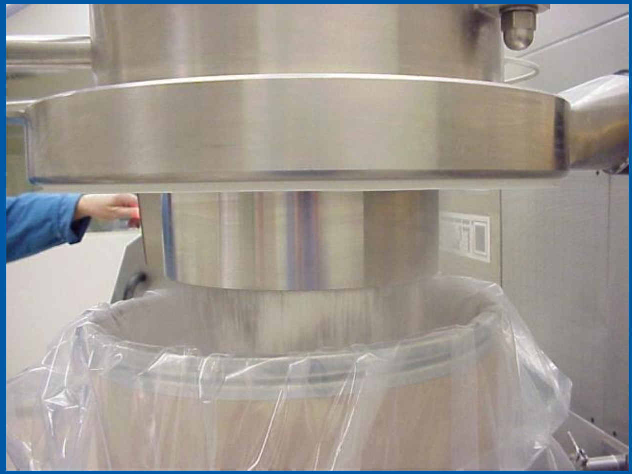
U.S. National Nanotechnology Initiative, NanoEHS strategy, 2011

Manufacturing

EXPOSURE SCENARIOS

Highest potential for exposure in the workplace is related to the use of unbound nanoparticles and nanofibers in either dry or liquid formulation

- Maintenance of production systems
- Pouring and mixing operations
- Nanoparticle generation in non-enclosed systems
- Handling powders
- Cleaning of dust collection systems and spills



EXPOSURE SCENARIOS

Potential for exposure to respirable-size particles containing nanomaterials in the workplace also exists during mechanical disruptions of composites and coatings containing nanomaterials

- Machining
- Sanding
- Drilling
- Cutting

EXPOSURE MEASUREMENT

Multiple tools are needed to assess exposure:

- Mass
- Size distribution and number
- Surface area

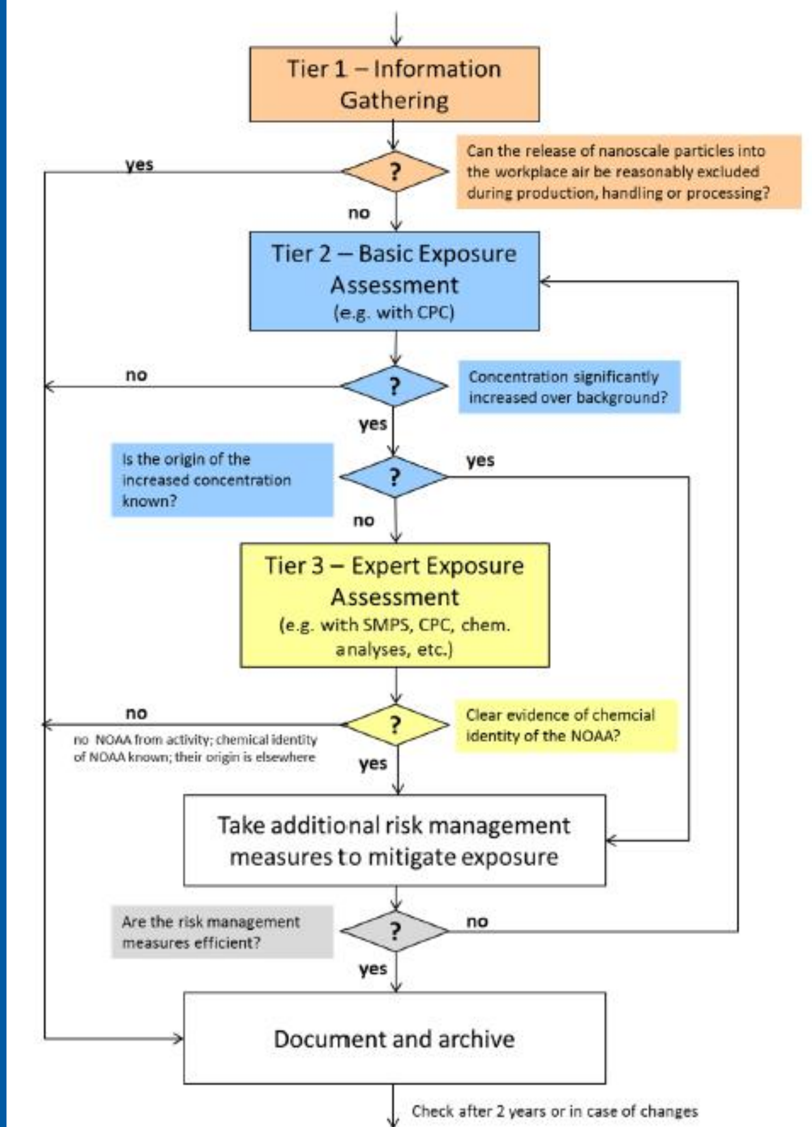
Sampling techniques for measuring airborne nanoscale aerosols (ultrafines) exist

Background measurements are necessary

Real-time exposure measurements can be used to characterize effectiveness of controls

TIERED APPROACH TO EXPOSURE ASSESSMENT

- Integral element of standard industrial hygiene approaches
- 3 Tiers
  - Tier 1: Information gathering
  - Tier 2: Basic exposure assessment
  - Tier 3: Expert exposure assessment
- Assessment of particle number concentration
- Review of existing, mass based data on nuisance dust recommended



WORKPLACE EMISSIONS

- Single-wall carbon nanotubes peak levels in lab-scale production = 53 µg/m^3 (Maynard et al. J Tox Env Health 2004)
- Multi-wall carbon nanotubes peak levels in lab-scale production = 430 µg/m^3
- Metal oxides peak levels in manufacturing facilities = 4000 µg/m^3

Occupational exposure to nanosilver

End-point	Value/characteristics	Method
Exposure situation	Silver nanoparticles <100 nm in size using a large-scale pilot reactor, daily production amount; 5 kg/day	dry ICP method manufacturing
Materials used	Silver nanoparticles ranging from 20 to 30 nm were manufactured from precursors (silver wire, powder, and liquid) which were introduced to the reactor using a ICP torch and reacted with acetylene and oxygen gases.	
Emission levels	Mass (3.7-4 h): 0.02-0.102 µg/m³ (Ag) (LOD = 0.15 ppb; LOQ = 0.51 ppb) Number(6 h): Indoor: 534.6-6,657 particle/cm³ (average diameter: ~100 nm, range 15-710 nm) In side of the collector: 25,022-2,373,309 particle/cm³ (average diameter: ~30nm, range 15-710 nm)	Mass concentration with NIOSH 7300, Number concentration using DMAS (SMPS) in real time
Inhalation Exposure		
Personal exposure – 8h TWA	0.102 µg/m³ (159 min, 315.8L) 0.12 µg/m³ (160 min, 315.2L)	NIOSH 7300-ICP method

Occupational exposure to nanosilver

Human data				
	TSP*(mg/m³)	Air Ag (µg/m³)	Blood(µg/dL)	Urine(µg/dL)
Personal -1 (Male/42age ,7yr)	0.15755	0.35	0.034	0.043
Personal -2 (Male/37age ,7yr)	0.10869	1.35	0.030	ND

*TSP – Total Suspended Particulate

NOAEL AgNP = 133 µg/m^3 (3x10^6 particle/cm^3)

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Exposure Assessment Case-Study: Nanogold

S. Africa

(slides provided by Dr. Mary Gulumian, NIOH)

Human exposure

- Project initiated in 2012
- Site specification
    - Pilot-scale facility for R&D laboratory
    - Quantities produced: 100 mL – 100 L
- Particles produced
    - Citrate stabilized 14 and 40 nm, synthesized by the Turkevich method.

Methodology

- Synthesis process reviewed to identify potential sources of emissions
- A walk through to determine the emission containment measures and also processes/tasks that may require air sampling
- Exposure assessment through area sampling of particle number concentration

Particle emission assessment

- Area sampling
  - Hand held particle counters
  - Desk-top particle counters
- Personal sampling
  - Personal samplers with MCE filters and flow rate of 2L/min
- Off-line particle characterisation
  - Nano-ID for particle collection
  - ICP-MS, TEM, FE-SEM

Personal exposure – 8h TWA

- Depending on tasks performed:
  - 0.000281 µg/m^3 - 0.0158 µg/m^3

- NOAEL (NOEL):
  - 2.36 × 10^5 particles/cm^3 (=0.38 µg/m^3)
- LOAEL (LOEL):
  - 1.85 × 10^6 particles/cm^3 (=20.0 µg/m^3)

Sung et al. Subchronic inhalation toxicity of gold nanoparticles. Particle and Fibre Toxicology 2011, 8:16

Consumer products

Nanomaterials in consumer products

Nanomaterial	Consumer products
Carbon nanotubes (CNT)	Electronic devices, sports equipment, composite plastics
nano-silver (nanoAg)	Textiles, anti-bacterial kitchenware
Carbon Black (CB)	Tires, printing toner, plastics
nano titanium dioxide (nanoTiO2)	Paints, coatings, composite plastics
nano-silica (nanoSiO2)	Coatings, composite plastics, tires
nano zinc oxide (nanoZnO)	cosmetics, coatings and paints
nano titanium nitride (TiN)	PET-bottles
nano iron oxides (nanoFeO/Fe2O3)	Electronic devices
nano cerium oxide (nanoCeO2)	Fuel additive
nano phosphates (nanoLiFePO4)	Li-Batteries

Emission of nanomaterials from consumer products

	Value/characteristics	Method
Emis. levels	Amount of silver leached into liquid media 1) plush toy - interior foam (48.2 ± 5.0mg Ag/kg) -saliva: 1.77 ± 0.03 mg Ag/kg product -sweat: 18.5 ± 1.1 mg Ag/kg product urine: 17.4 ± 0.8 mg Ag/kg product 2) plush toy - exterior fur (0.6 ± 0.1 mg Ag/kg) -saliva: 0.03 ± 0.001 mg Ag/kg product -sweat: 0.14 ± 0.002 mg Ag/kg product -urine: Not Detected 3) baby blanket (109.8 ± 4.1 mg Ag/kg) -saliva: 1.2 ± 0.1 mg Ag/kg product -sweat: 4.8 ± 0.3 mg Ag/kg product -urine: 3.7 ± 0.3 mg Ag/kg product -saline: 4.0 ± 0.0 mg Ag/kg product	The leaching assays consisted of soaking product samples in relevant liquid media under various conditions related to normal use. The leaching media included tap water; synthetic sweat, saliva, and urine; milk formula; and orange juice. Pieces of products of 0.5 g were placed in a 100-mL beaker and enough liquid media was added to achieve a 1:50 mass ratio between the product mass and leaching media. The soaking time depended on each product's intended use and type of liquid media (see Ref. 16 for details). When soaking was completed, 10-mL aliquots were removed from the leachate, 10% nitric was added to dissolve any silver particles present, and the leachate was analyzed for silver content using inductively coupled plasma mass spectrometry (ICP-MS) with detection limit of 0.5 ppb.

Emission of nanomaterials from consumer products

4) Sippy cup 1 - rubber ring (24.3±2.9mg Ag/kg)
- milk formula: Not Detected
- orange juice: 0.41 ± 0.01 mg Ag/kg product

5) Sippy cup 1 - cap (9.4 ± 1.0 mg Ag/kg)
- milk formula: Not Detected
- orange juice: 0.07 ± 0.01 mg Ag/kg product

6) Sippy cup 2 - spout cover (2.1±1.5 mg Ag/kg)
- milk formula: 0.93 ± 0.02 mg Ag/kg product
- orange juice: Not Detected

Amount of silver transferred from surfaces onto dermal wipes:

1) baby blanket: 23.0 ± 1.4 μg/m²
2) plush toy: exterior 13.8 ± 8.4 μg/m²
3) disinfecting spray 9.0 ± 2.8 μg/m²
4) surface wipes 2.3 ± 0.2 μg/m²
5) kitchen scrubber 0.3 ± 0.1 μg/m²

The tabletop humidifier emitted 2.3 ± 0.7 ppb of silver in the condensed vapor, while the manual humidifier did not emit detectable levels of total silver.

Ambient aerosol concentrations were not significantly elevated above background levels (~3–6 × 10^3 cm^{-3} for aerosols 14–750 nm and <150 cm^{-3} for aerosols 0.3–10 μm in diameter) during product use.

NIOSH Method 9102: Elements on Wipes that specifies the use of ASTM E 1792-01 benzalkonium chloride moist towelettes was used to evaluate skin exposures. In this swipe method, the sampled surface is swiped three times using overlapping “S” patterns with horizontal and vertical strokes. Towelettes were digested in HNO_3 and H_2O_2 and analyzed for silver content by ICP-MS.

To evaluate release from humidifiers, The water reservoir of each humidifier was completely filled with tap water and left at room temperature for 5–6 days. Water samples from each basin were collected, acidified with 10% HNO3, and analyzed by ICP-MS.

To assess the total silver concentration in the vapor produced by each humidifier, the humidifier reservoirs were filled with tap water and left for 3 days. Using PVC reducing pipe and tubing, the outlet of each humidifier was routed through a sealed beaker submerged in ice, to promote condensation inside the beaker (~20 mL). The condensate was then acidified with 10% HNO_3 and analyzed by ICP-MS.

Concentrations and size distributions of aerosols 14–750 nm in diameter were measured using a scanning mobility particle sizer (SMPS 3936, TSI). Larger aerosols (300 nm–10 μm in diameter) were measured using an optical particle counter (Aerotrak, TSI).

Emission of nanomaterials from consumer products

- Hand dryer having a filter coated with silver nanoparticles: 150-200 particles/cm^3, which is significantly lower than background aerosol level in indoor environment (~5,000 to 10,000 particles/cm^3)
- Hair irons coated with or without silver nanoparticles: 40,000 particles/cm^3 when either hair iron was operated
- Face mask coated with silver nanoparticles: 5 particles/cm^3 when continuous air jet was impinged

Waste management

WASTE MANAGEMENT: RECYCLING

RECYCLING

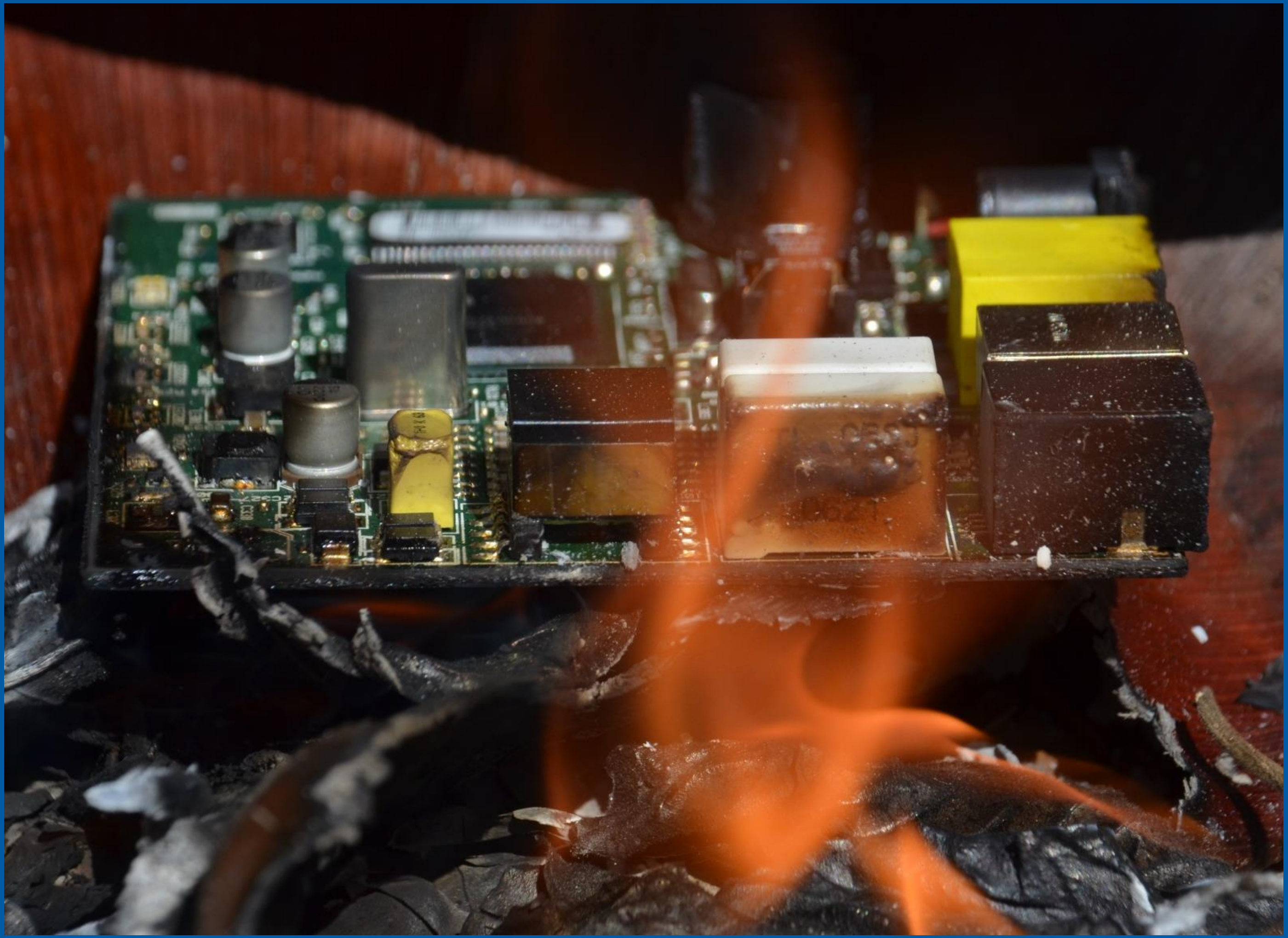
- The main concern about possible risks of waste containing nanomaterials (WCNM) in recycling processes are nano-objects that might be released into the workplace atmosphere, or into the environment by way of the air, water and or soil

- Information about the fate of nanomaterials in recycling processes is only beginning to emerge. Mostly, exposure scenarios are based on modelling, and not on evidence.

RECYCLING

- Potential risks of exposure depend on the specific recycling processes and may be to nano-objects:
  - emitted during transport, sorting , shredding, grinding or pouring of the WCNM
  - in liquid media (water, solvents) due to cleaning or rinsing the products before mechanical recycling
  - set free in the flue gas or to the ambient air with thermal processes (heating, welding, pyrolysis)

WASTE MANAGEMENT: INCINERATION



INCINERATION

- (Re-)formation or destruction of NMs during incineration:
  - destroyed due to combustion (e.g. CNT to CO_2)
  - not destroyed or incinerated, but captured by the flue gas treatment system (e.g. metal oxides)
  - not be destroyed during combustion, but with other substances and form new particles (e.g. $CaCO_3$ to CaO and CO_2)
  - Bigger particles turn into new, smaller particles
  - Agglomeration/aggregation into bigger particles

INCINERATION

- So far only few studies investigated nanomaterial emissions from municipal solid waste incinerators.
- According to those a high end flue gas treatment system may be able to remove most nanomaterials from the flue gas. However, this was only shown for certain materials or calculated on a model base.
- E.g.: 0.00058 wt-% of the sludge and waste incineration fly ash is smaller than 100 nm.

WASTE MANAGEMENT: LANDFILLING

LANDFILLING

- It is estimated that up to 50% of three commonly used NMs produced by weight (nano-silver, nano-titanium dioxide and carbon nanotubes) will end up in landfills (Mueller and Nowack, 2008). Most are as nanocomposites.

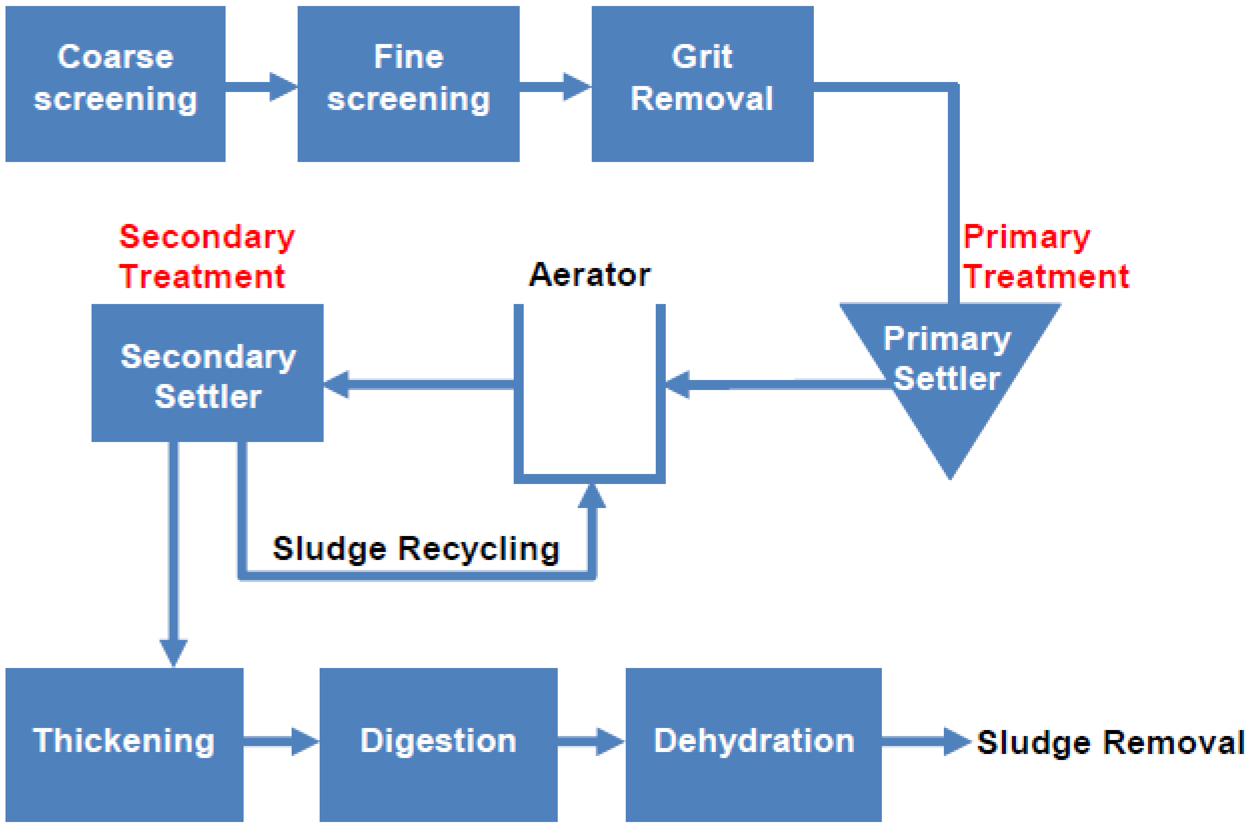
- A recent study by Hennebert *et al.* (2013) of NM in landfills found a significant amount of colloids (dispersed phase in the size range of 1nm-1µm) in leachate, different in elemental composition from natural ones.

LANDFILLING

- The fate of NMs will most likely be a function of the mobility of the nanoparticles, their degradability and the degradability of the host material: solid composite vs. liquid suspensions.

- Some NMs may be subject to degradation and/or that they may be released from a nanoproduct under landfill conditions, depending on the nature, location and quality of the NM bonds.

WASTE MANAGEMENT: SEWAGE



Source: from ADEME (2004): www.ademe.fr

SEWAGE TREATMENT

- Conventional wastewater treatment plants can effectively remove NMs such as nano-silver, nano-zinc oxide, nano-cerium dioxide, nano-titanium dioxide (Ag°, ZnO, CeO_2 and TiO_2) from wastewater; however, the NMs typically accumulate (> 90%) in the waste sludge or biosolids (Westerhoff et al., 2013).

SEWAGE TREATMENT

- Chemical transformations in sewage treatment plants, such as dissolution by reduction (e.g. CeO_2) or oxidation (e.g. Ag°), are important parameters to be taken into consideration in nanomaterial balances. These chemical transformations are accompanied by precipitation in the form of mineral species such as Ag_2S or $CePO_4$ which are thermodynamically stable and less toxic than the original materials.
- Surface functionalization in order to incorporate nanomaterials into consumer products may slow down these transformations and maintain the initial oxidation or reduction state for longer by limiting contact with bacterial aggregates.

Environmental exposure to nanosilver

End-point	Value/characteristics	Method
Exposure situation	Release of nanosilver from textiles intended for domestic uses: Environmental exposure scenarios for nanosilver consider the washing of textiles in domestic homes and the release of wastewater to WWTPs. Data on ecotoxicological effects and environmental fate of the nanosilver NM300-K (material 2) as well as data on emission data for nanosilver from textiles were derived from a German joint research project called UMSICHT. Emission data consider the concentrations of nanosilver released from three different textile types (cotton, polyester, lyocell cellulose fibre) upon standardized washing processes (DIN EN ISO 105 C12-2S) at differing temperatures. Maximum release rates were used for a conservative scenario. Concentrations of nanosilver for sewage sludge and PECs of nanosilver for the environmental compartments surface water, sediment and soil (after sewage sludge application) were deduced. For the derivation of PECs an exposure approaches have been used considering the emission based on technological process data: Emissions of nanosilver from textiles into WWTP per inhabitant and day: Scenario A (cotton): 312.5 $\mu g \cdot inh^{-1} \cdot d^{-1}$ Scenario B (polyester): 162.5 $\mu g \cdot inh^{-1} \cdot d^{-1}$ Scenario C (lyocell fibre): 21.9 $\mu g \cdot inh^{-1} \cdot d^{-1}$	Calculations are based on the ECHA Guidances on Information Requirements and Chemical Safety Assessment and technological process data, e.g. weight of laundry, fraction of nanosilver-containing textiles per washing, nanosilver emission from nanosilver containing laundry, assumed washing per day, no. of washing machines per inhabitant.

Environmental exposure to nanosilver

Waste Water Treatment Plant		
Exp. level	<u>Effluent: Predicted Concentration</u> Scenario A (cotton): 0.156 µg/L Scenario B (polyester): 0.081 µg/L Scenario C (lyocell fibre): 0.011 µg/L <u>Sludge: Predicted Concentration</u> Scenario A (cotton): 3.96 mg/kg_{dw} Scenario B (polyester): 2.06 mg/kg_{dw} Scenario C (lyocell fibre): 0.28 mg/kg_{dw}	Assuming 10 000 inhabitants per WWTP, volume of 200 L waste water per day and inhabitant, fraction of 10 % of nanosilver remaining in the effluent and 90% of nanosilver in the sewage sludge and sludge rate of 710 kg/d
Surface Water		
Exp. level	Predicted Environmental Concentration Scenario A (cotton): 15.63 ng/L Scenario B (polyester): 8.13 ng/L Scenario C (lyocell fibre): 1.09 ng/L	Assuming fraction of 10% of nanosilver remaining in the effluent, volume of 200 L waste water per day and inhabitant and 10fold dilution of waste water in the receiving water body
Sediment		
Exp. level	Predicted Environmental Concentration Scenario A (cotton): 4.08 $µg/kg_{dw}$ Scenario B (polyester): 2.12 $µg/kg_{dw}$ Scenario C (lyocell fibre): 0.29 $µg/kg_{dw}$	Using arithmetic mean of retention coefficients for investigated nanosilver in soils of 257.7 L/kg and assuming volume fraction of water in suspended matter of 90%, of suspended matter of 10 %, density of solid phase of 2500 kg/m^3, bulk density of suspended matter of 1150 kg/m^3 and conversion factor sediment to sediment of 4.6
Soil		
Exp. level	Predicted Environmental Concentration Scenario A (cotton): 6.62 $µg/kg_{dw}$ Scenario B (polyester): 3.44 $µg/kg_{dw}$ Scenario C (lyocell fibre): 0.46 $µg/kg_{dw}$	Assuming application rate of $sludge_{dw}$ of 5 tons/hectare in 3 years (according to the sewage sludge regulation (AbfKlärV), soil density of 1.5 g_{dw}/cm^3 and soil depth of 0.2 m

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Nanomaterial Exposure Standards

EXPOSURE RELATED STANDARDS

OECD (www.oecd.org/science/nanosafety/)

- OECD Compilation of guidance on emission assessment for nanomaterials
- Compilation and Comparison of Guidelines Related to Exposure to Nanomaterials in Laboratories
- Report of an OECD Workshop on Exposure Assessment and Exposure Mitigation: Manufactured Nanomaterials

EXPOSURE RELATED STANDARDS

U.S. NIOSH (www.cdc.gov/niosh/topics/nanotech/)

- Approaches to Safe Nano (www.cdc.gov/niosh/docs/2009-125/)
- Exposure to carbon nanotubes and nanofibers (www.cdc.gov/niosh/docs/2013-145/)
- Exposure to titanium dioxide (www.cdc.gov/niosh/docs/2011-160/)
- Engineering controls of nanomaterials (www.cdc.gov/niosh/docs/2014-102/)

EXPOSURE RELATED STANDARDS

ISO (TC229, www.iso.org/iso/iso_technical_committee?commid=381983)

- TR12885:2008 – health and safety practices in nanotechnology workplaces
- TS12901-1:2012 – occupational risk management
- TR13329:2012 – preparation of material safety data sheets (MSDS)
- TS13830:2013 – labelling of consumer products containing nanomaterials
- TS12901-2:2014 – control banding for nanomaterials

Conclusions

- Some limited data on nanomaterial emissions in the workplace and to consumers from products containing nanomaterials exists. However, personal exposure data are still very limited.

- Environmental exposure data are limited to modelling.

- The main technical challenge is the lack of standardized protocols for exposure measurements.

Future activities in nanomaterial exposure

- Expanding to consumer and environmental exposures
- Focus on exposure guidelines

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www.cdc.gov/niosh/topics/nanotech

"The findings and conclusions in this presentation have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy."

Hazard Assessment

HAZARD ASSESSMENT

- **Incidental nanoparticles**
  - –Workplace exposures (welding fumes, diesel exhaust)
    - Reduction of lung function, adverse respiratory symptoms, and suppression of defense responses
  - –Air pollution epidemiology
    - Cardiovascular diseases
      - – ischemic and thrombotic effects
      - – inflammatory effects, platelet aggregation in animals
    - Brain inflammation and plaque formation

Size

Shape

Surface

HAZARD ASSESSMENT

- **Manufactured nanoparticles**
  - –Animal studies showed
    - Inhaled nanoparticles can enter the blood stream and translocate to other organs
    - equivalent mass doses of insoluble nanoparticles are more potent than large particles of similar composition in causing pulmonary inflammation and lung tumors
    - changes in the chemical composition, crystal structure, and size of particles can influence their oxidant generation properties and cytotoxicity

Size

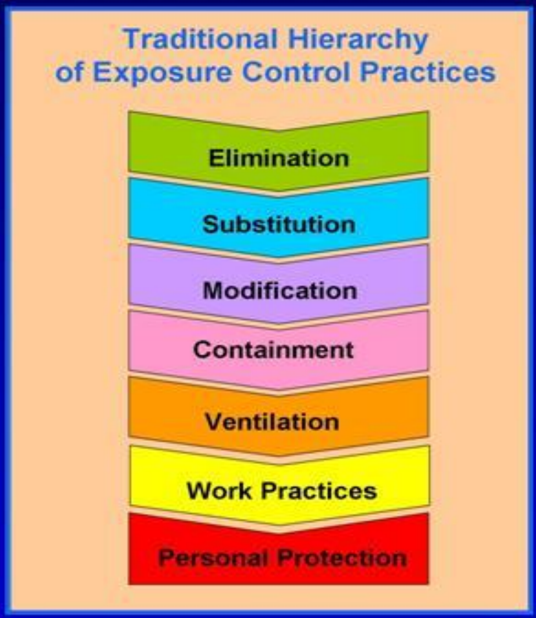
Shape

Surface

Exposure Mitigation

EXPOSURE MITIGATION

Hierarchy of Controls



- Eliminate the hazard, where possible
- Substitute less hazardous materials
- Engineering solutions preferred
- Modify the material or process
- Control as close to source as possible
- Administrative and personal protective controls less desirable

EXPOSURE MITIGATION

Workplace risk management program for nanomaterials

- Evaluating the hazard posed by the nanomaterial based on available physical and chemical property data, toxicology, or health-effects data
- Assessing the worker's job task to determine the potential for exposure
- Educating and training workers in the proper handling of nanomaterials
- Establishing criteria and procedures for installing and evaluating engineering controls at locations where exposure to nanomaterials might occur
- Developing procedures for determining the need for and selecting proper personal protective equipment

Systematic re-evaluation of hazards and exposures is critical

EXPOSURE MITIGATION

Prudent measures to minimize worker exposures

- For most processes and job tasks, the control of airborne exposure to nanomaterials can be accomplished using a variety of engineering control techniques similar to those used in reducing exposure to general aerosols.
- The use of good work practices can help to minimize worker exposures to nanomaterials. Examples of good practices include cleaning of work areas using HEPA vacuum pickup and wet wiping methods, preventing the consumption of food or beverages in workplaces where nanomaterials are handled, providing hand-washing facilities, and providing facilities for showering and changing clothes.

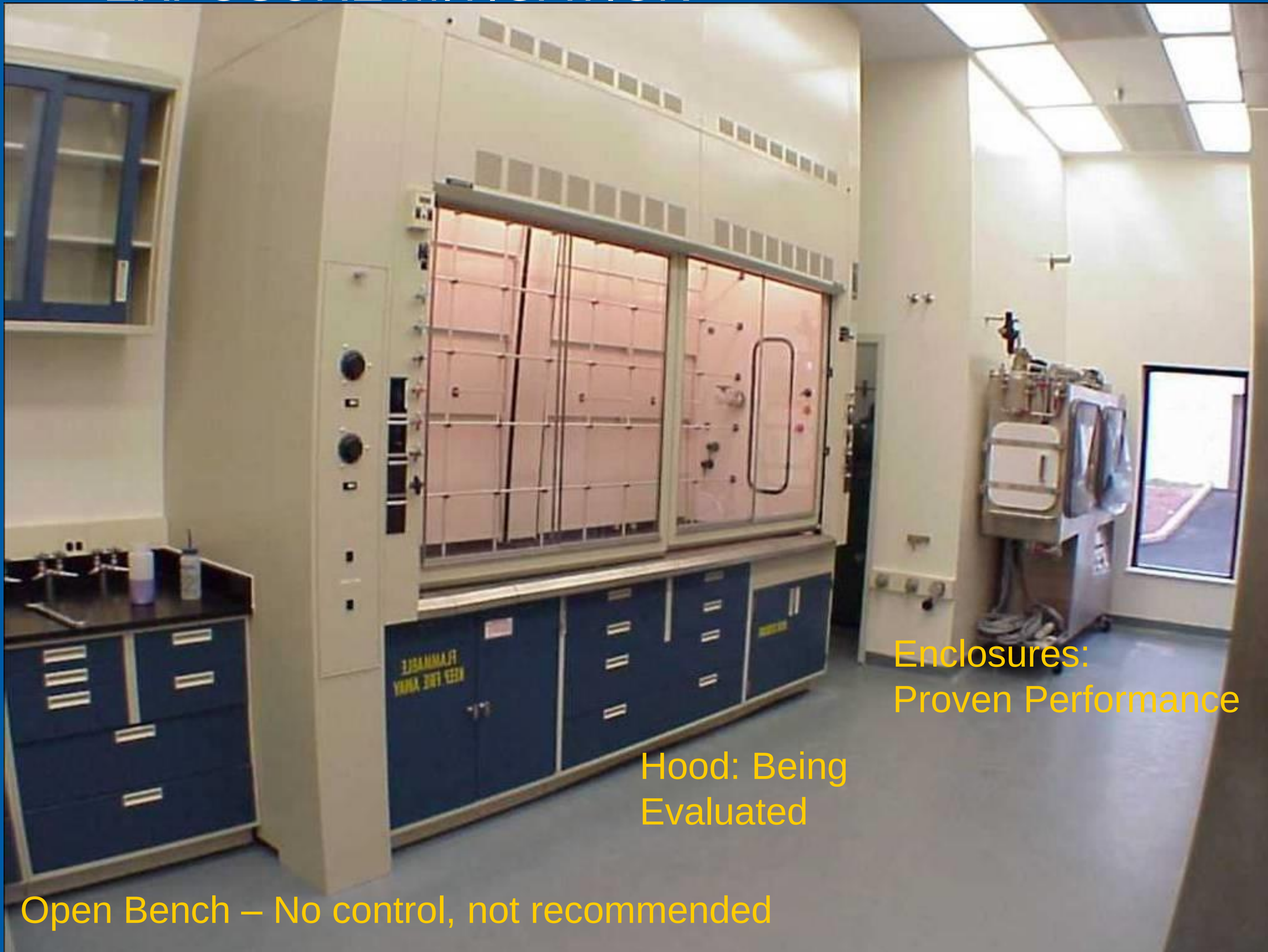
Occupational health surveillance is an essential component of an effective occupational safety and health program

EXPOSURE MITIGATION

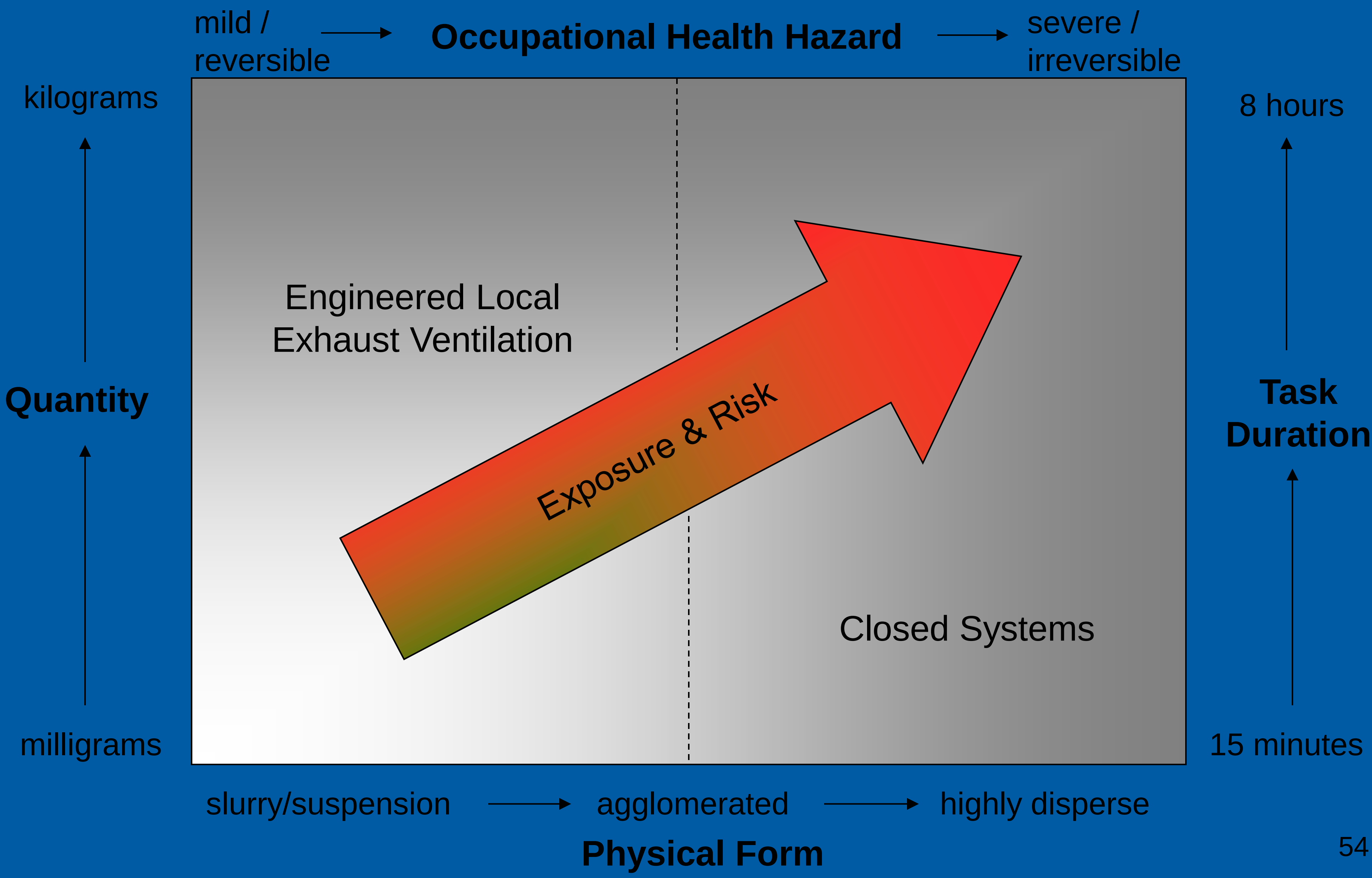
Engineering controls

Control Technology	Anticipated Performance
Open handling with engineered local exhaust ventilation	< 1000 μg/m^3
Directional laminar flow with LEV and Vacuum conveying	10 μg/m^3 – 1000 μg/m^3
Closed systems	1- 10 μg/m^3
High-containment	< 1 μg/m^3

EXPOSURE MITIGATION



EXPOSURE MITIGATION



EXPOSURE MITIGATION

Respirators

- Certified respirators provide stated level of protection
- Use of respiratory protection for nanomaterials - professional judgment and hazard assessment