#### Critical parameters/data needs for exposure assessment in occupational and environmental scenarios

Session 4 (Day 2): How relevant are model nanoparticles to understanding exposure in the workplace

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Joint EU-US Workshop, Washington, 10-11 March 2011





WORLD HEALTH ORGANISATION COLLABORATING CENTRE FOR OCCUPATIONAL HEALTH IOM and nano

NANETS

- 120 staff, Edinburgh HQ
- Research, consultancy, training in occupational and environmental health, hygiene, risk
- Fully independent 1990 no core or support funding
- Charitable status not for profit
- Mission "For the benefit of those at work and in the community"
- Independent Authoritative Impartial



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- Nanoparticles: An occupational hygiene review (HSE)
- A scoping study to identify hazard data needs for addressing the risks presented by nanoparticles and nanotubes (Defra)
- Refnano Recommendations on key Reference Materials
  for nanotoxicology (Defra)
- Guide to Safe Handling & Disposal of Engineered Nanomaterials (BSI 6699-2)
- Cell Pen Nanoparticle Translocation Review (Defra)
- HARN High Aspect Ratio Nanoparticle Review (Defra)
- EMERGNANO Emerging Evidence Review (Defra)
- RIPoN2 and RIPoN3 (COM)



## Overview

- Measurement and measurement issues
- Plausible and actual exposure "situations"
- Characteristics of these situations, experience from current work
- Use of model particles
- Current European activity
- Conclusions



# Multiple reasons for measurement

- Identification of sources of nanoparticle emissions;
- Quantification of release
- Assessment of the effectiveness of any control measure implemented
- Ensuring compliance with any OEL or self-imposed (in-house) exposure standard;
- Evaluation of exposure scenarios, eg for REACH
- Support to exposure modelling
- Assessment of exposed populations in an epidemiology study
- Different approaches are required for different situations



#### Measurement data

- Occupational
  - Concentration in air (mass, number, surface area)
  - Size distribution in air (mass, number, surface area)

- Environment
  - Release rates into a compartment (air, water, soil) (kg/day)
  - Release factors (%)
  - Concentration within a compartment
  - Transfer between compartments
  - Size distribution in compartments



## Exposure assessment data

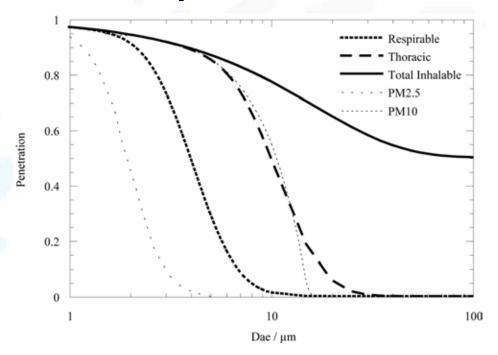
- Exposure assessment is not just concentration measurement. Information required about ...
  - Route
  - Magnitude
  - Duration
  - Frequency
  - Distribution spatial
  - Distribution (within worker between worker)
  - Control measures .....





# Conventional assessment of airborne exposure to particles

- Measurement of mass concentration (mg/m<sup>3</sup>)of health related fractions in the workers breathing zone
- Inhalable, thoracic, respirable fractions ISO 7708 (1995)
- Based on personal sampling
  - Wide range of personal samplers available
    - IOM inhalable sampler, 37mm sampler, cyclones
- All of these devices could be used but would not tell anything about the nano-fraction





## Specific challenges with nano

- What are the characteristics of possible exposure?
- What metric should be used for measuring nanoparticle exposure?
- Can we discriminate nanoparticles and other nano-objects from background aerosol?
- How can we use size information and what is the maximum size we should measure?
- Can HARN such as CNT or nanowires be measured using methods for, or derived from, or analogous to current methods for fibres?
- Linking concentration measurements to personal exposure
- What methods are available?

E.g. Maynard and Aitken 2007

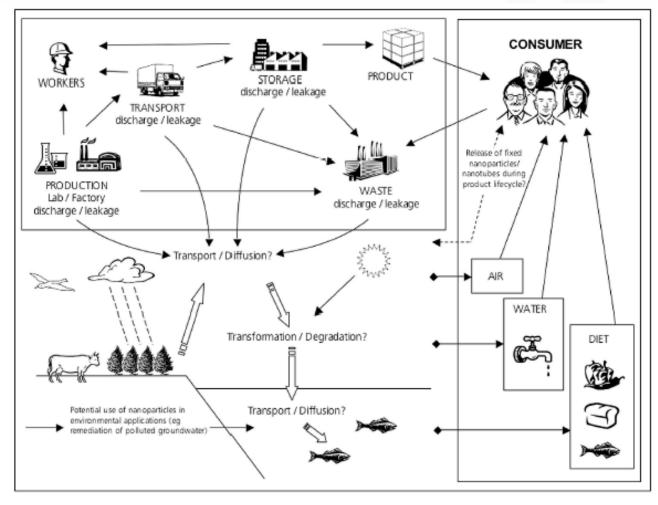


## Hypothetical scenarios of NP production and use

time

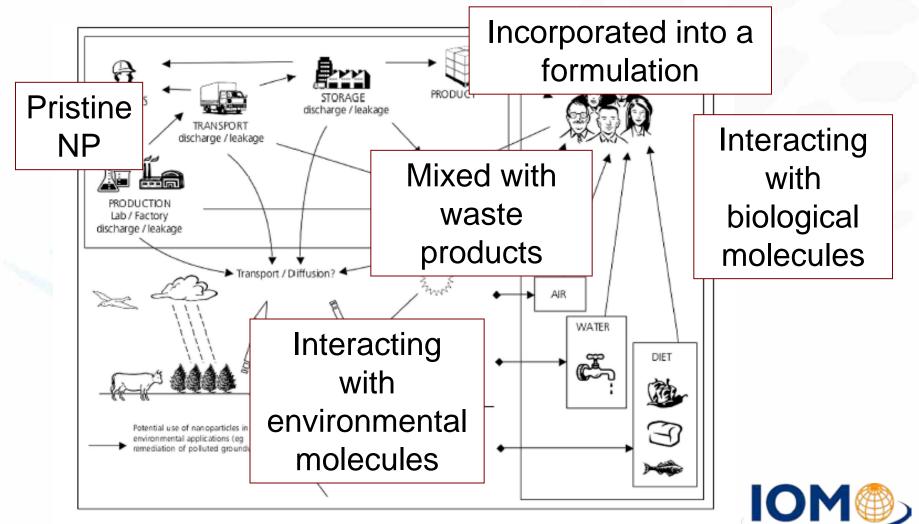


#### **Exposure scenarios**



RS Report Nanoscience and nanotechnologies (2004)

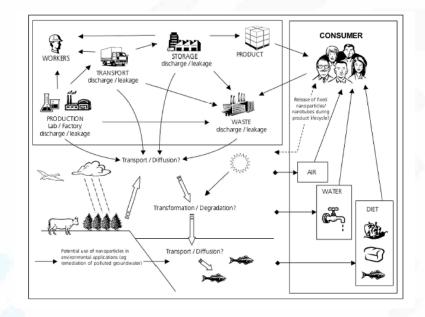
#### **Exposure scenarios**



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## Scenarios

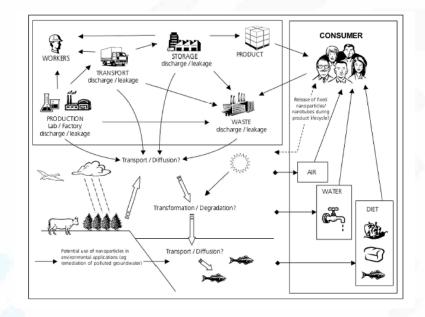
- Synthesis scenarios
  - Synthesis process
  - Handling, bagging
  - Maintenance
- Applications scenarios
  - Incorporation into a formulation or matrix
    - Mixing (+ handling, bagging, maintenance)
- Usage scenarios
  - Use of formulation
    - E.g. painting, spraying, coating
  - Use of composite of matrix
    - E.g. Cutting, sawing, drilling, finishing
- Disposal scenarios





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2004	2004	2006	2007	2007	2008	2008	2008	2008	2008	2008	2008	2009	2009	2009	2009	2009	2009	2010	2010	
Kuhlbusch	Maynard	Kuhlbusch	Hsu	Methner	Bello	Demou	Fujitani	Han	Tsai	Tsai	Yaganeh	Bello	Demou	Park	Peters	Plitzco	Tsai	Johnson	Gohler	
						-														Materials
x		х					_											Х		СВ
							х				х							Х	1	Fullerenes
			х			х			х	х			х	х	х	х			х	Metal/metal oxides
				х												х				CNF
	х																х			SWCNT
	1				х		N	х				х					х	Х		MWCNT
																				Scale
x	х	х				х	х				х			х	х	х				Industrial
	х		х	х	х			х	х	х		х	х				х	Х	х	Laboratory
									-											Tasks/processes
	1	х			х	х					х		х	х	х	х	х			Synthesis
	х				х															Recovery
х							х													Bagging
	х	х	х	х	х			х	х	х	х			х	х	х		Х		Handling/processing
				х								х							х	Sawing/sanding composite
	х						х				х					х				Cleaning
	х						х													Deliberate agitation



#### Examples

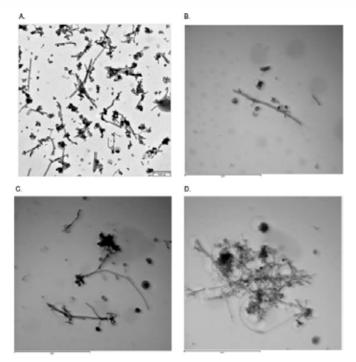
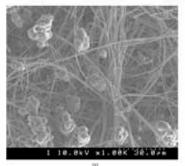


FIG. 2. Shapes of MWCNTs. The bars in (B) and (C) indicate 4 μm. (A) MWCNTs sampled after opening of the furnace. (B) Individual tube structure. (C) Multiple tube structure. (D) Clumped tube structure.

> Han *et al*, Inhalation Toxicology,20:741-749, 2008 Mixing CNT, preparing a composite 197 f/ml\* (all less than 1.5 mm)





Fujitani *et al* (2008). Measurement of the physical properties of aerosols in a fullerene factory for inhalation exposure assessment. Journal of Occupational and Environmental Hygiene; 5: 380-389.

REARE 7. Following particles: (a, b) REA images, of surgest solucied during the substanduring the bacartar constant. Note that aplatter was tool a surgest procedure.



J Nanopart Res (2009) 11:231-249 DOI 10.1007/s11051-008-9499-4

NANOPARTICLES AND OCCUPATIONAL HEALTH

#### Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes

Dhimiter Bello · Brian L. Wardle · Namiko Yamamoto · Roberto Guzman deVilloria · Enrique J. Garcia · Anastasios J. Hart · Kwangseog Ahn · Michael J. Ellenbecker · Marilyn Hallock

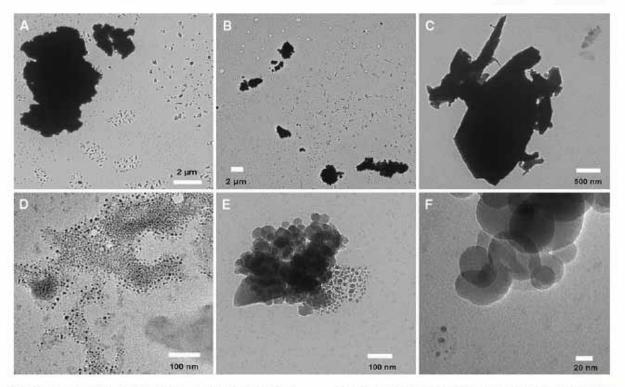


Fig. 7 Representative TEM images of samples collected during dry cutting of various composites illustrating: a wide range of particles (A, B); particles with very complex morphologies common to all composites (C); abundance of 10–20 nm particles on all composites; a typical enlargement of agglomerates and large particles such as those in image B (F). Images (A) and (C) originated from dry cutting of base-carbon composites, (B) from CNT-alumina composites, whereas (D-F) from CNT-carbon composites



# Possible classes of nanoparticles

A. Spherical homogeneous

- 0.999 0.999 0.999
- D. Agglomerate homogeneous



B. Fibrous homogeneous

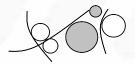
E. Heterogeneous concentric



C. Non-spherical homogeneous

- Heterogene
- F. Heterogeneous distributed

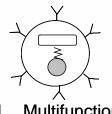
Maynard and Aitken 2007



G. Heterogeneous agglomerate



H. Active particle



 Multifunctional particle



## Can model particles be used to assess exposure

Probably not

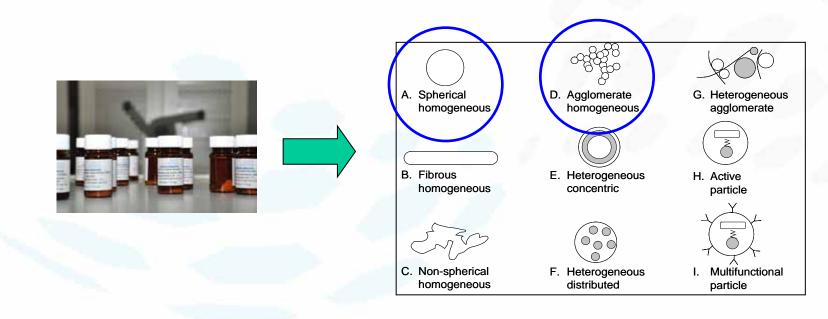


## Model particle applications

Development and calibration of instruments for air	Aerosol dispersion					
Development and calibration of instruments for water	Liquid dispersion					
Efficacy of control measures e.g. respirators, filters	Aerosol dispersion					
Efficacy of control measures e.g. gloves	Powder or liquid dispersion					
Simulation of work activities	Power, aerosol or liquid dispersion					
Dustiness testing	Powder					
Release from composites	Surface coating or solid dispersion in composite					
Interactions with "background" particles	Aerosol or liquid dispersion					
Relationship between metrics	Aerosol or liquid dispersion					
Transfer between compartments	Aerosol or liquid dispersion					
Validation of models	Aerosol or liquid dispersion					



### Requirements



- (Certified) Reference material or well characterised standards?
- Need is for dispersions with temporal stability in relation to size, aggregation state, concentration
- Traceable is also advantageous

IOM

## **European initiatives**







- Development of calibration facility for aerosol measurement instruments
  - www.nano-device.eu
- Nanomaterials repository, used in various FP7 projects and OECD
  - www.napira.jrc.ec.europa.eu
- Infrastructure for nanomaterials safety testing – Nanomaterials hub
  - www.qnano-ri.eu



- In addition, multiple FP7 tox and ecotox projects (e.g. ENPRA, MARINA) are developing dispersion protocols
- Characteristics, small quantities, presence of dispersants.
- How relevant are these for exposure studies



## Conclusions

- Still relatively few studies concerning exposure published (more emerging)
- Limited range of materials and tasks. Scenarios have mostly addressed synthesis processes and handling during production. Very few applications/downstream activities
- Most studies have found some evidence of exposure, often to much larger agglomerates
  - One study found clear evidence of "fibre-like" objects
- Categorisation approach potentially useful
- Model particles are not specifically useful in assessing exposure per se but have wide application in a range of development, modelling and simulation activities
- The key issue is dispersion in air or in liquid
- Some progress is being made



