Workplace & Experimental Studies on Exposure to Nano-objects; What have we achieved and what challenges remain?

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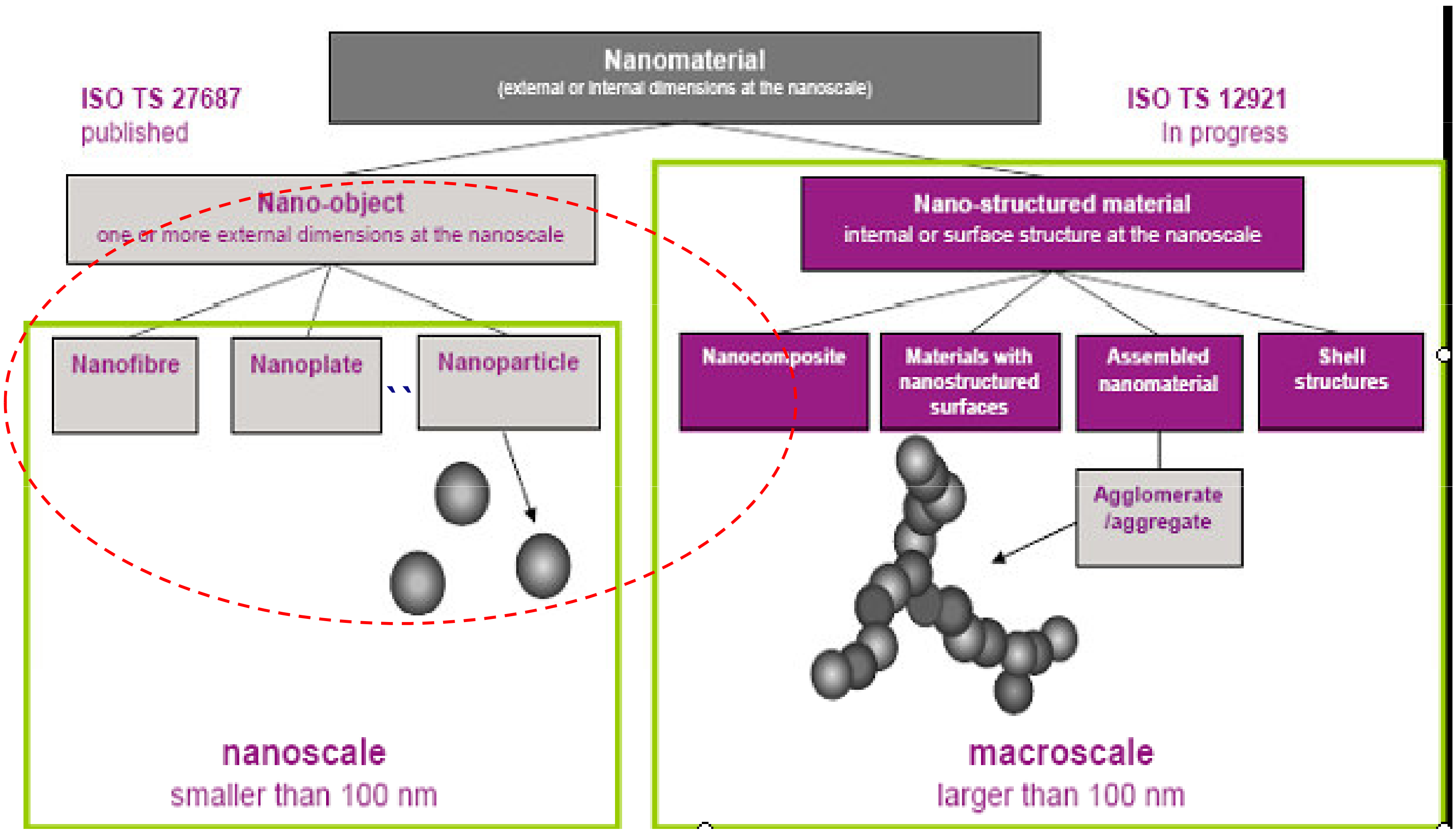
TNO | Knowledge for business

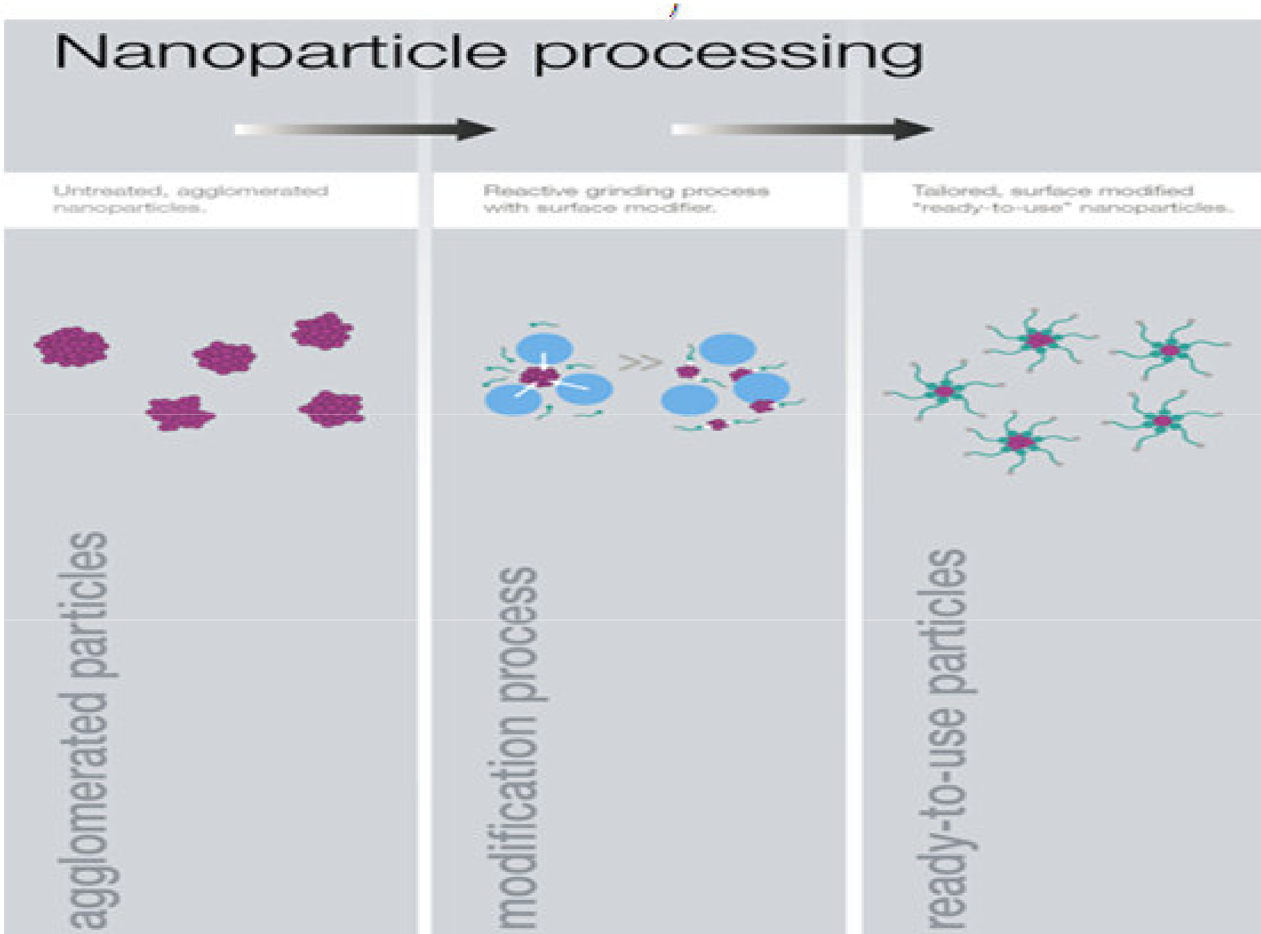
Outline

- Manufactured Nano Materials and situations with potential for emission / worker exposure
- Considerations for workplace air measurements and estimates for exposure
- Emission/ release of nano particles: conclusions from experimental studies
- Observations and preliminary conclusions from field studies
- Key issues for risk-relevant exposure assessment

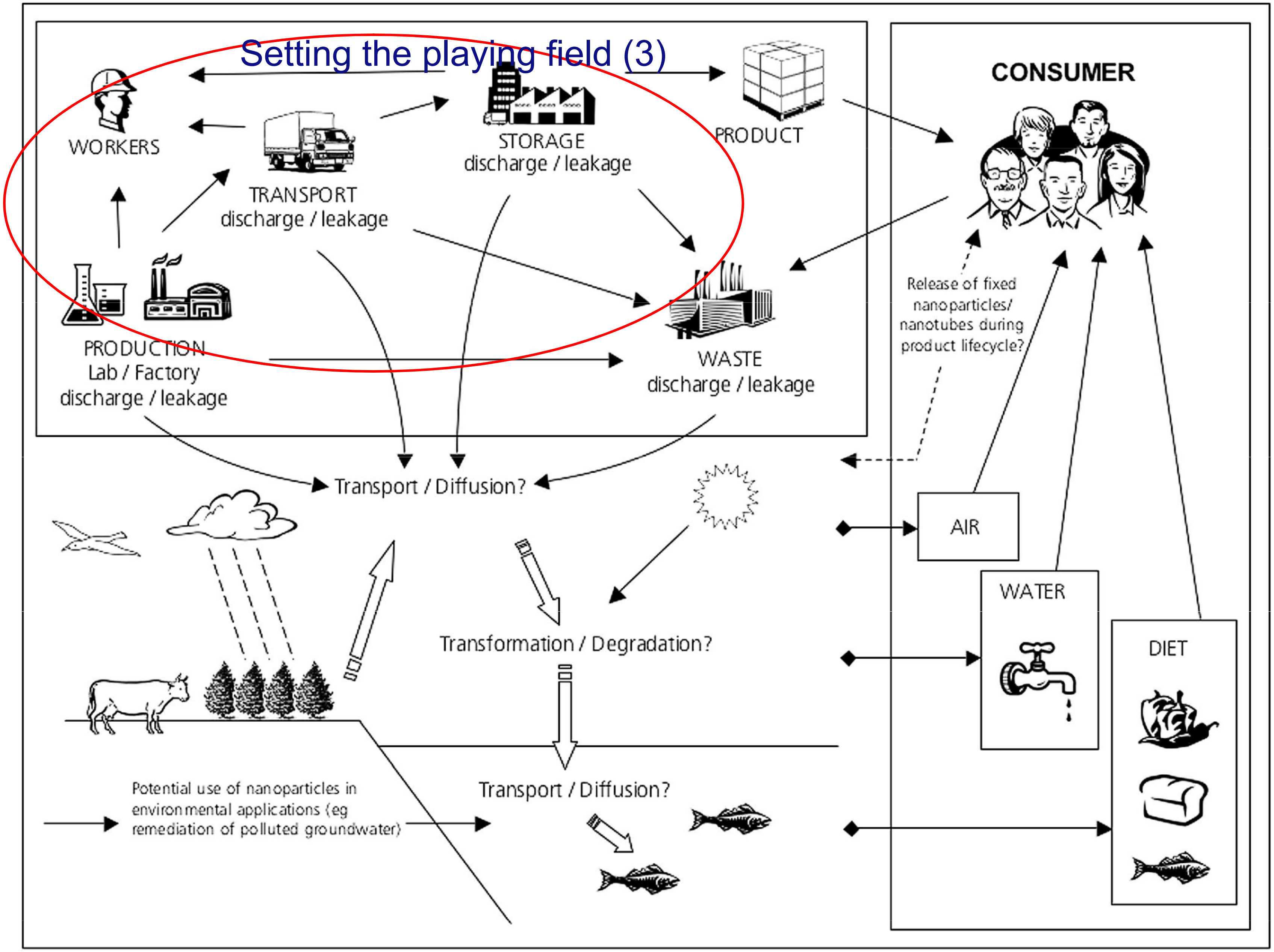
Setting the playing field (1)



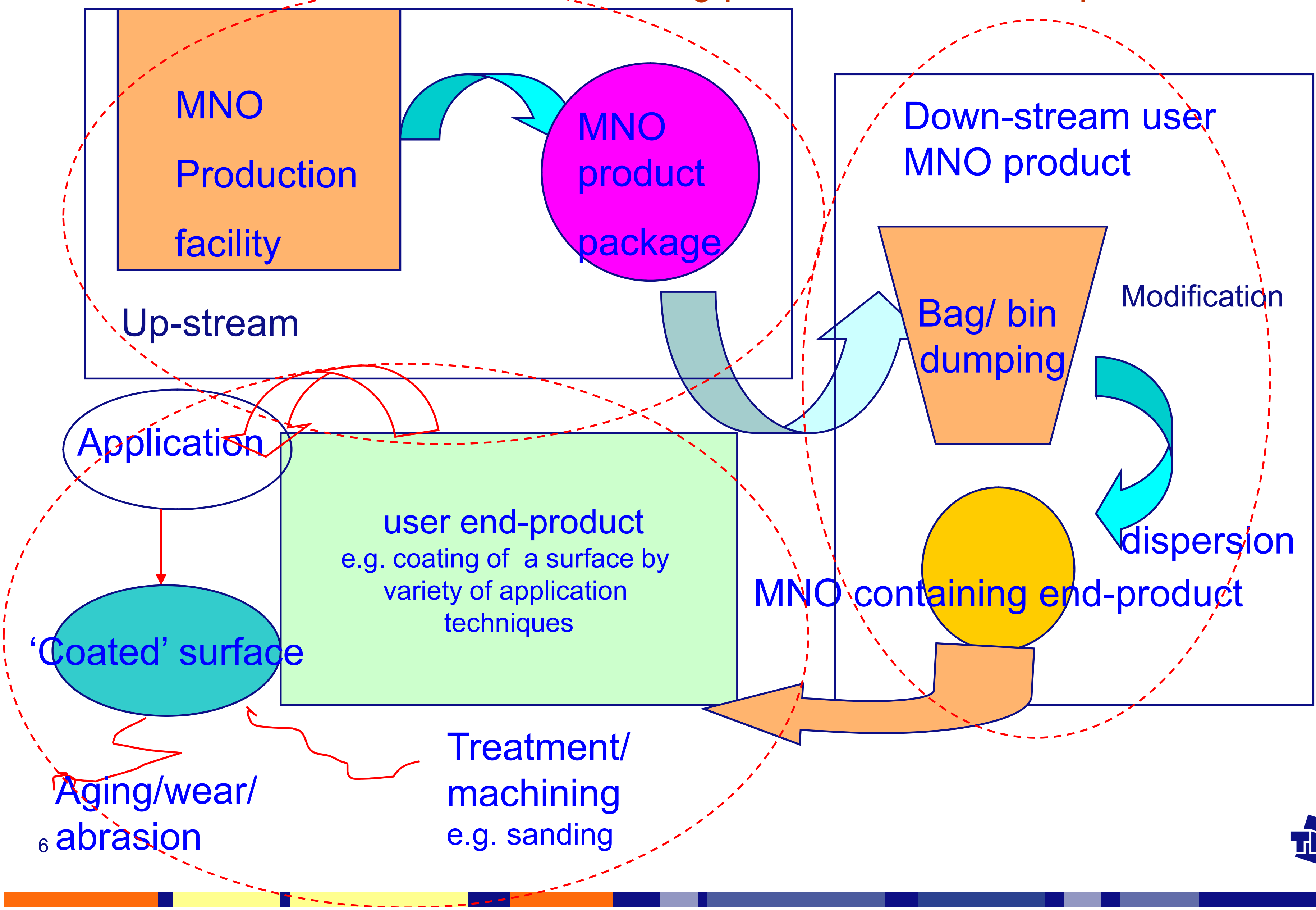
Setting the playing field (2)



Setting the playing field (3)



Potential for exposure to MNO in different exposure situations `MNO ‘embedded’ coating products as an example



Measuring concentration of MNO aerosols

- Would like to differentiate nano-sized aerosols from larger size fractions of same substance
  - Size-selective sampling

    YES (static/ metric)
- Would like to differentiate Manufactured nano objects (MNOs) from other NOs
  - (on-line/ direct) Identification

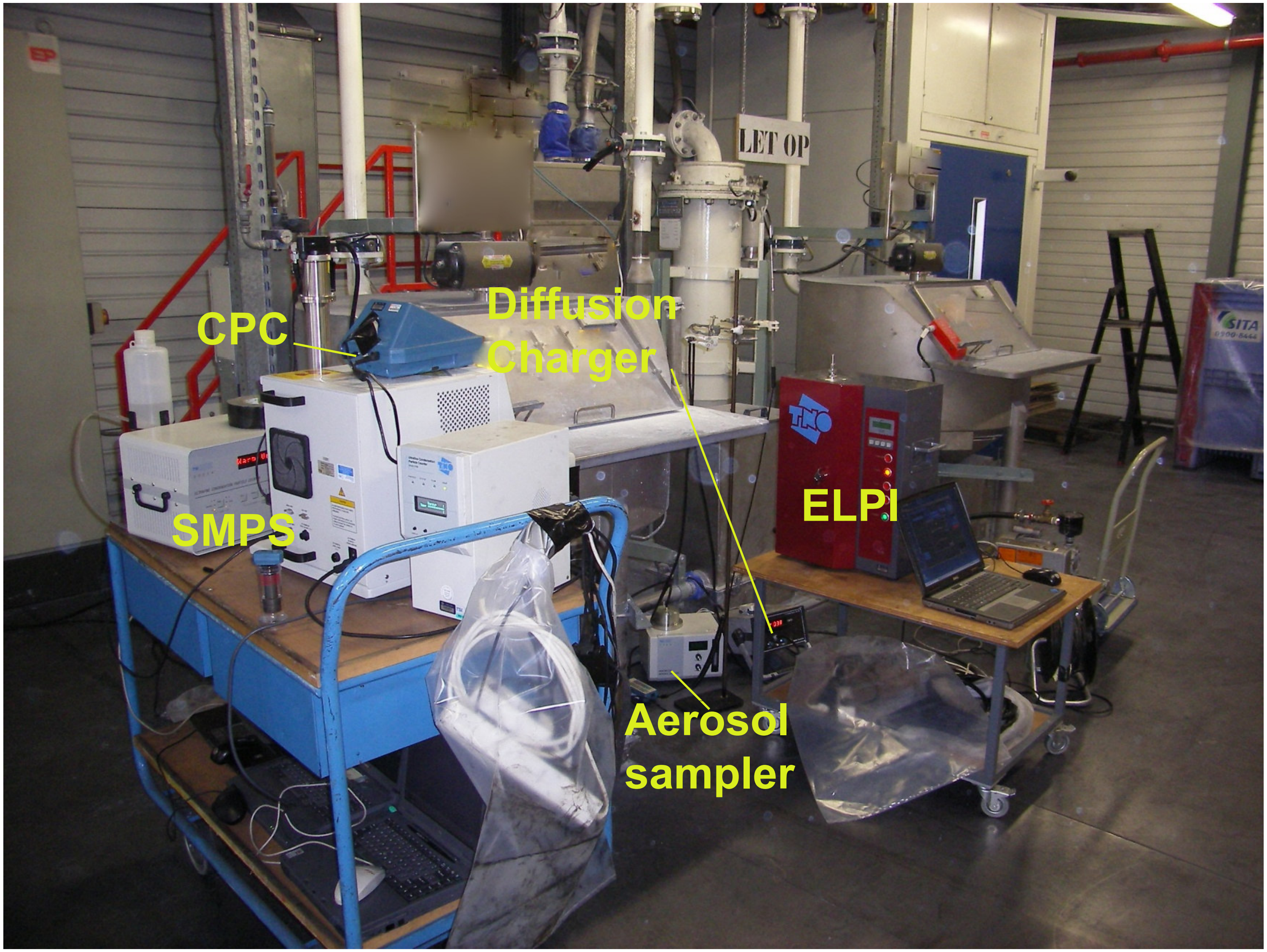
    NO (off-line)
- Would like to differentiate MNÒ-related activities from non MNO related activities
  - Sensitive instruments/ low detection limits /high resolution

    YES (robust/ static)
- Would like to measure different (exposure) parameters/ metrics e.g. number concentration (p/cm^3);mass concentration ($\mu g/m^3$); surface area concentration ($\mu m^2/cm^3$**)**
  - Multi-metric **personal** sampling instrument

    NO (various/ static)
- Would like to measure/calculate different exposure measures e.g average-, peak-, and cumulative concentration
  - (near) real-time measurements

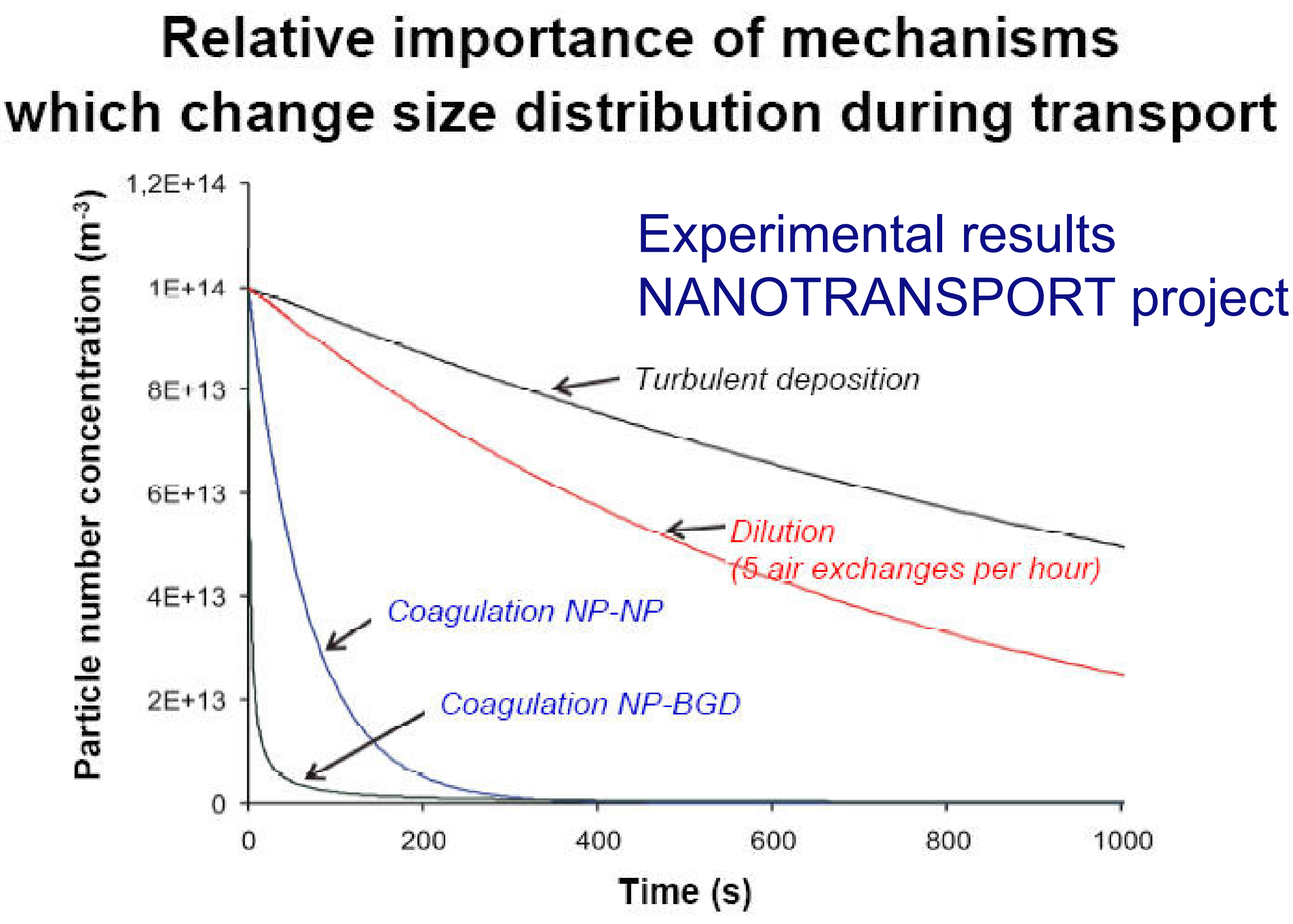
    YES (static)

Array of measurement devices



Experimental studies

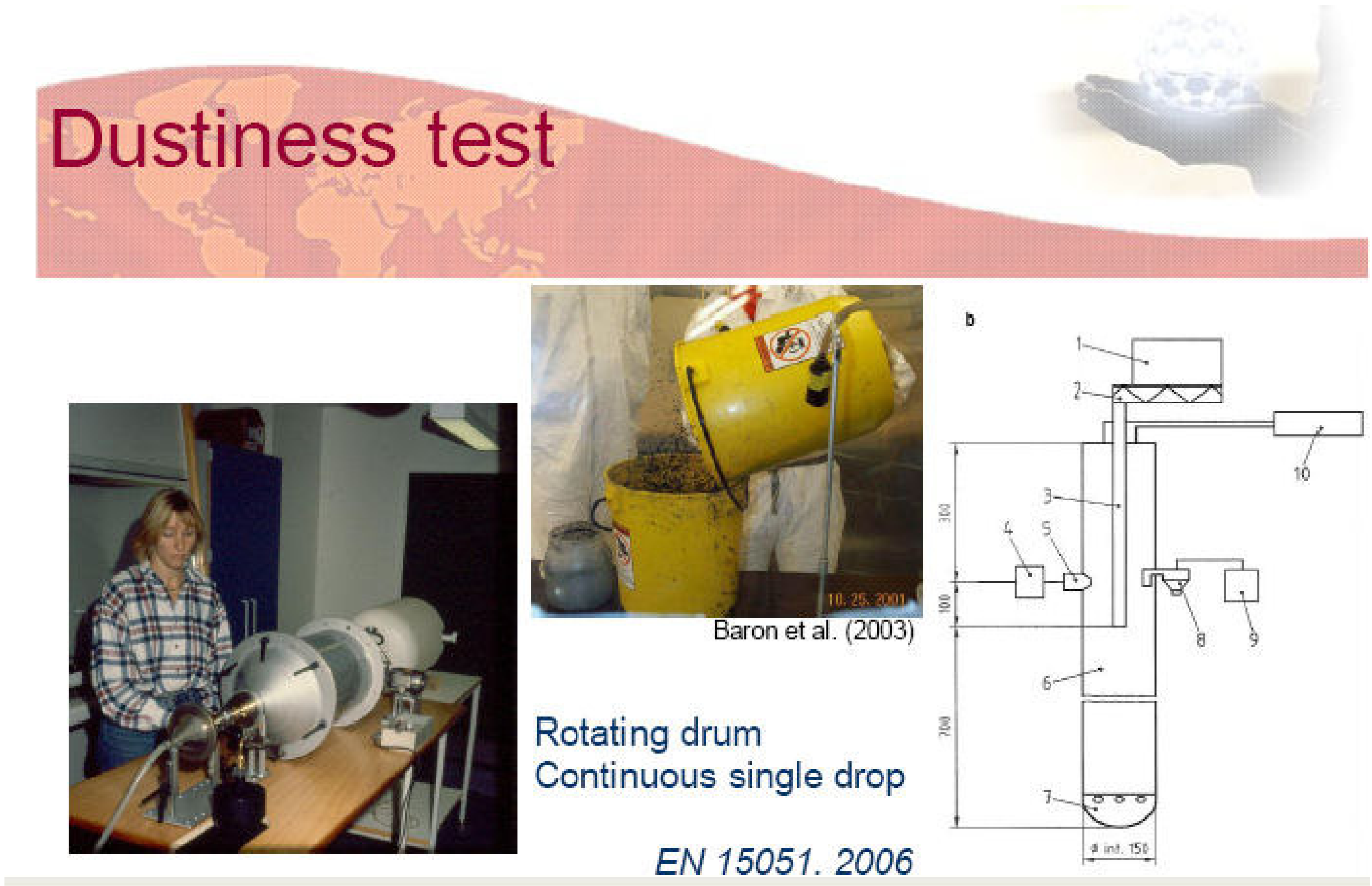
Processes following emission of primary NPs



Experimental results
NANOTRANSPORT project

Coagulation also depending on
Concentration and Size

EMISSION POTENTIAL during down-stream-use
Characterization of ‘bulk’/packaging MNO by dustiness testing

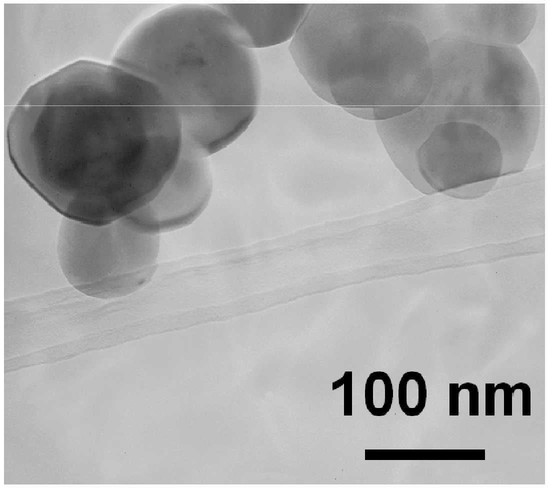


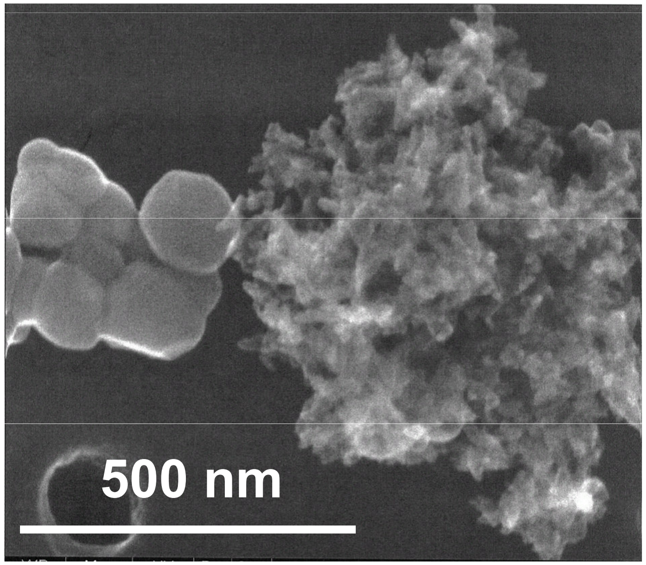
Dustiness of ”Micro-” vs NP powder

– an example using pigment and ultrafine TiO_2

Pigment grade TiO_2

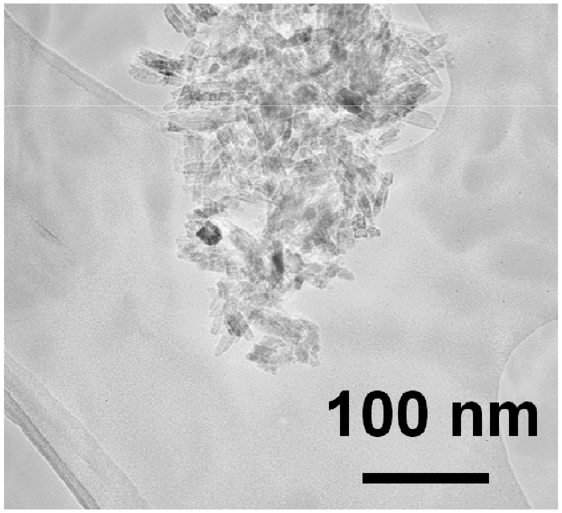
- ❑ **XRD-size: 170 nm**
- ❑ **BET-area: 10 m^2/g**





Ultrafine TiO_2

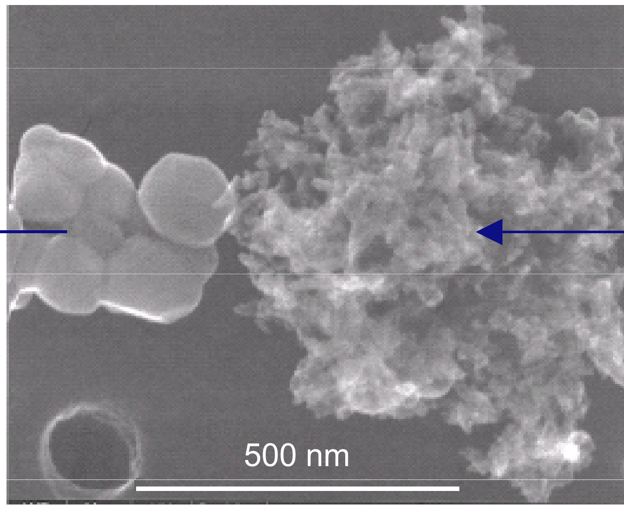
- ❑ **XRD-size: 18.6 nm**
- ❑ **BET-area: 100 m^2/g**



Images from Schneider et al. (2007) Nordic Ministry Council Report

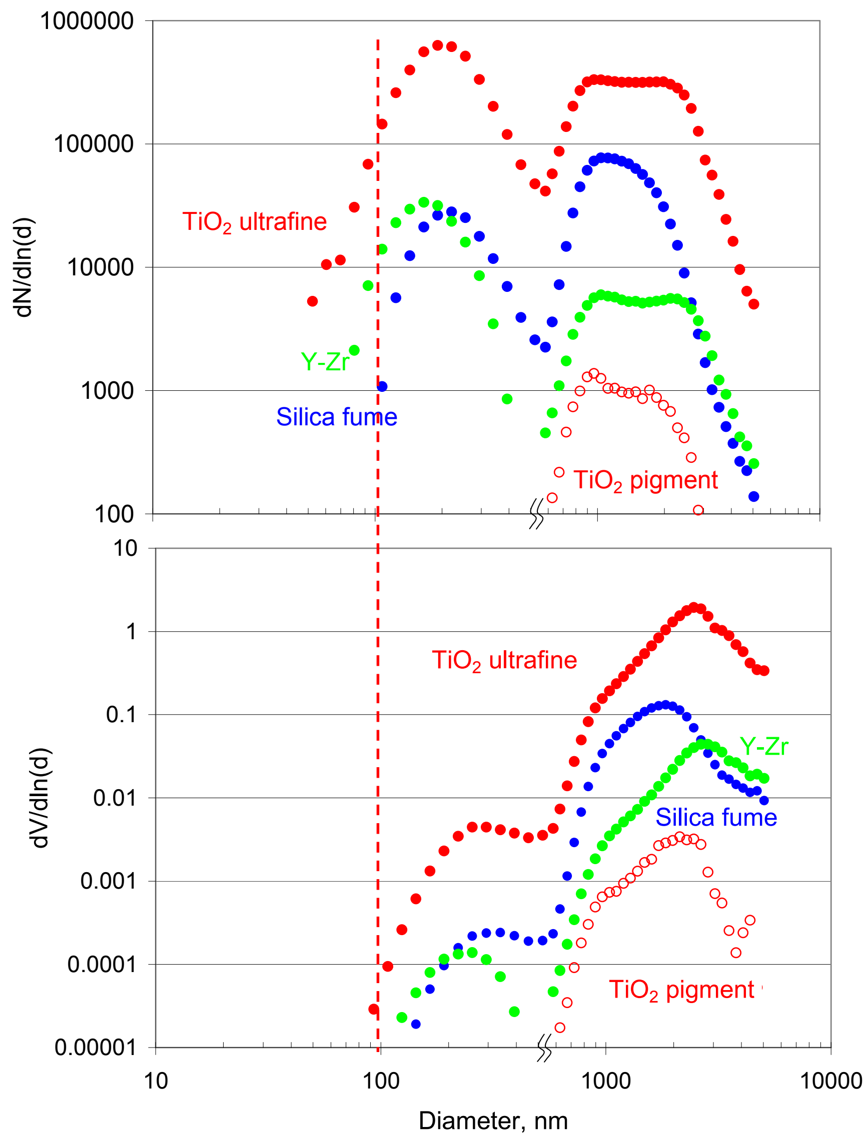
Dustiness of "Micro-" vs NP powder

– size distributions of pigment and ultrafine TiO_2



Dustiness

× 300

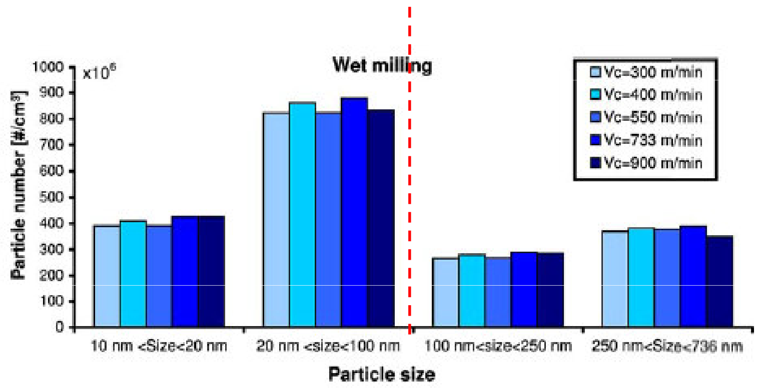


Data from Schneider T and Jensen KA (2008) Ann Occ Hyg.

Emission during (high energy) machining of substrates

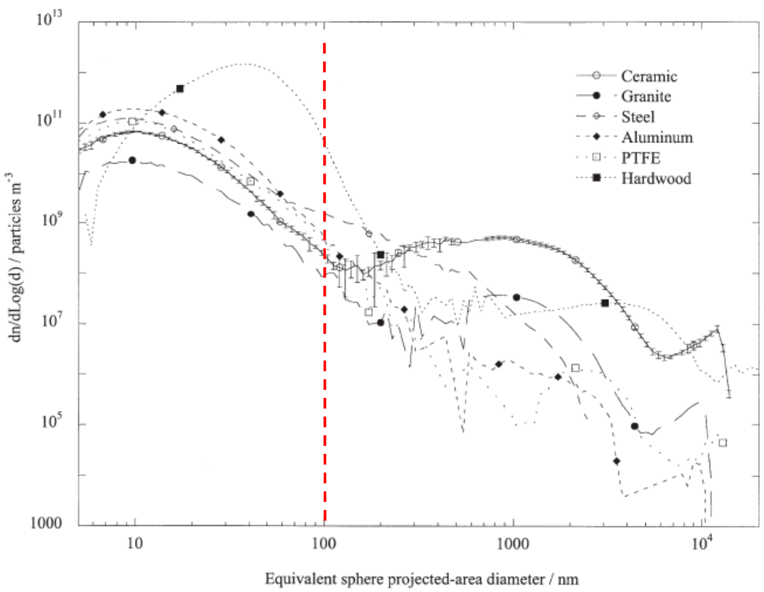
Zaghbani et al 2009:

High speed milling of Aluminum Alloy



Maynard & Zimmer (2002)

High speed grinding



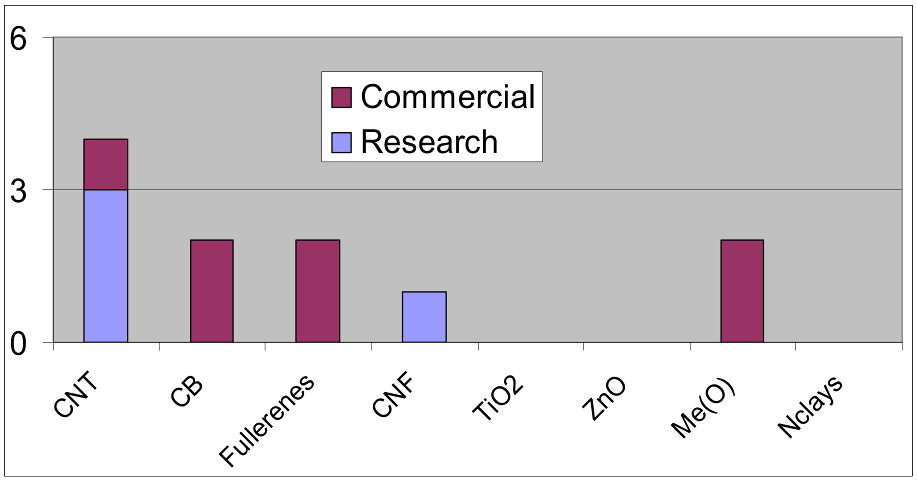
Conclusions on emission and transport processes from aerosol physics and experimental studies

- MNO production
  - Primary particles (if released) will rapidly coagulate
    - Agglomeration (similar aerosols/ loose binding)
    - Aggregates (similar and other aerosols/ firm binding)
    - Attached to/ scavenged by larger background aerosols

    (invisible in size distribution, but chemically identified)
- MNO handling of powders/ down-stream use
  - Distinct size modes, robust GMD
    - 200-300 nm (mobility diameter
    - > 1 µm (aerodynamic diameter)
  - Generally limited particle number concentration below 100 nm
  - Compaction reduces dustiness
- (High-energy) machining
  - Emission of particles in nano-size range
  - Energy, process and substrate depended

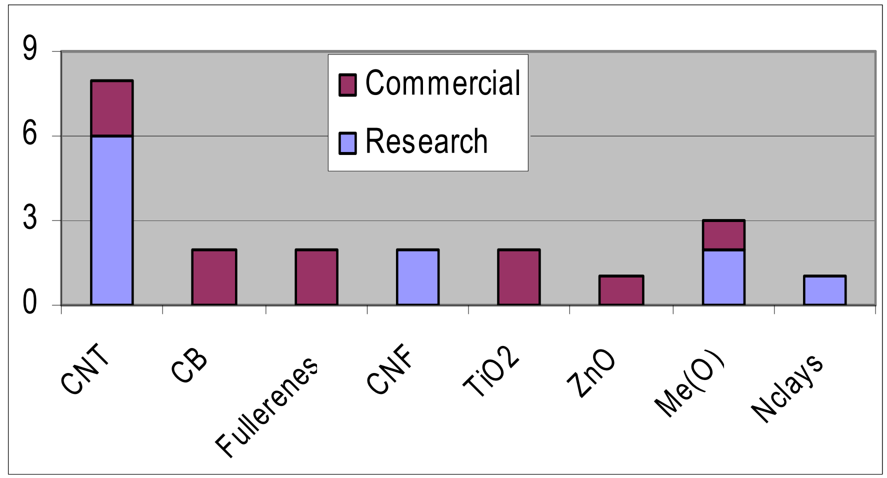
(~) Numbers of workplace air monitoring studies (02-2009)
Production of MNOs (research- commercial scale)

Peer reviewed (published+ in press)



Published + NANOSH

(NMP4-CT-2006-032777)

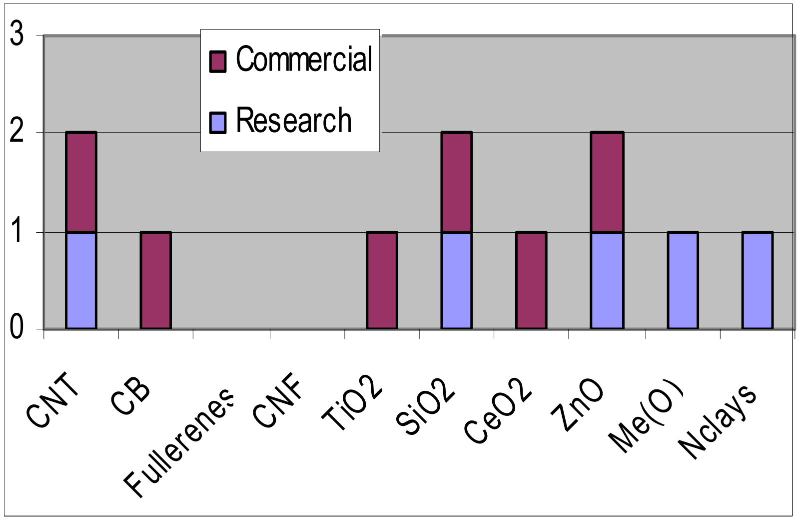


Kuhlbusch et al 2004, 2006; Maynard et al, 2004; Methner et al., 2007,

Methner 2008;Han et al, 2008; Yeganeh et al, 2008; Tsai et al, 2008ab, Bello et al, 2008; Demou et al, 2008;Peters, et al., 2009

(~) Numbers of workplace air monitoring studies (02-2009)

Down-stream use of MNOs (research- commercial scale)



Studies release of MNOs from MNO-containing (end)products

- Cutting CNT composites

(Bello et al 2008)

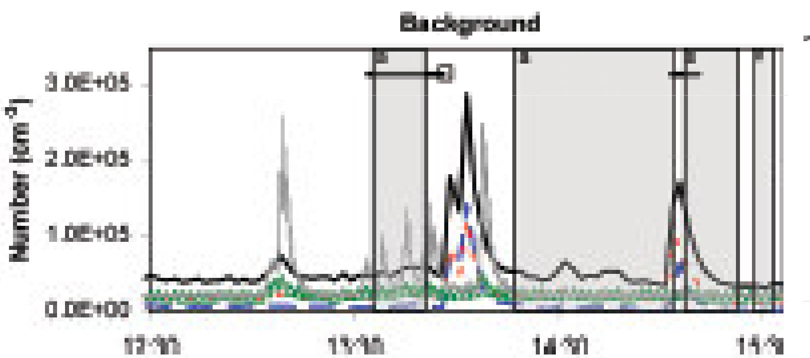
- Abrasion nano-coated surfaces

(Vorbau et al., 2009)

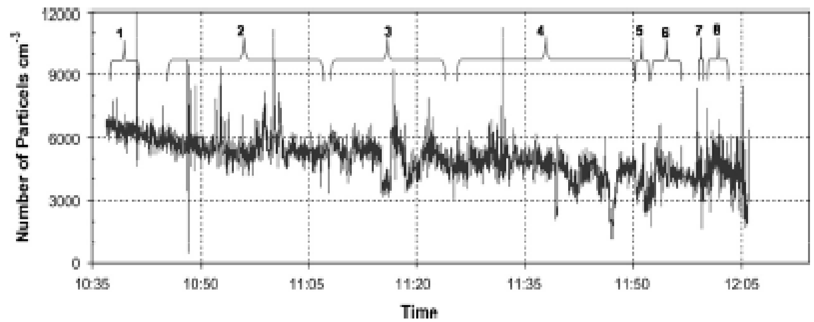
- Sanding nano-coated surfaces

(Koponen et al, NRCWE-Denmark; work in progress

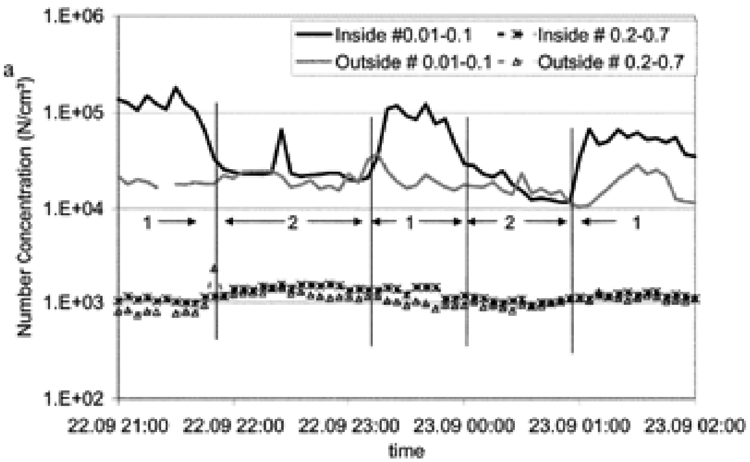
Results from workplace air monitoring studies
Examples of time/activity- concentration profiles



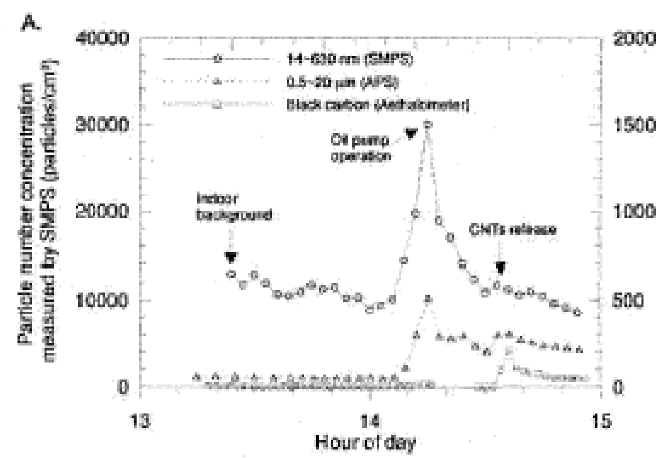
Yeganeh et al.,2008



Bello et al., 2008



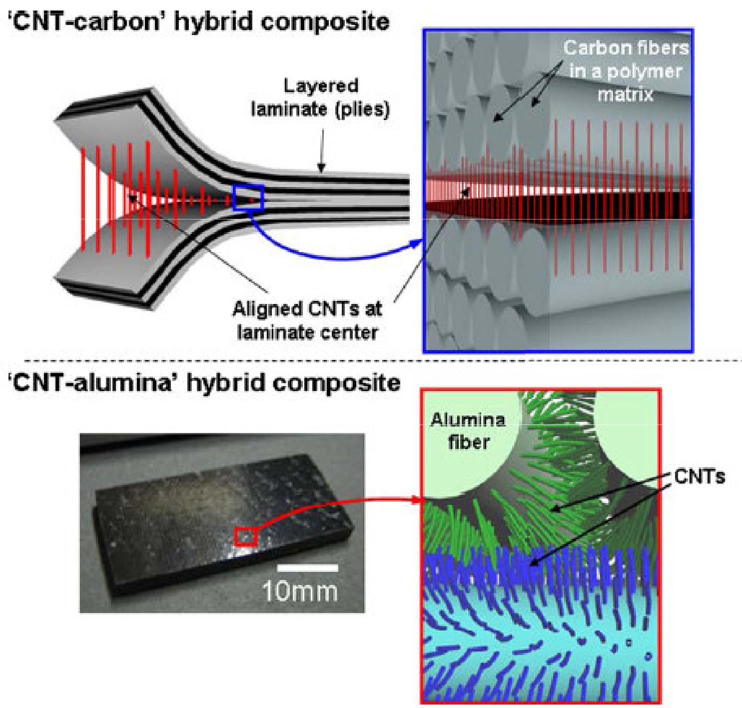
Kuhlbush et al., 2004

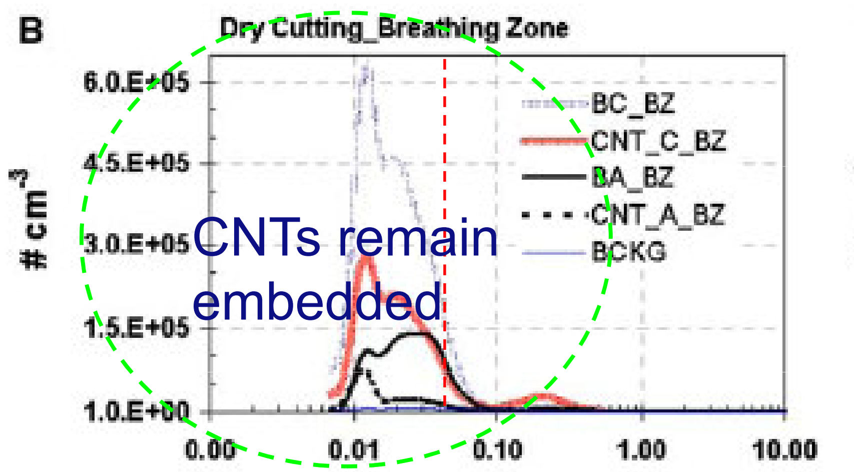


Han et al., 2008

Emission during ('Low energy) machining' of nanoparticles embedded products (`1)

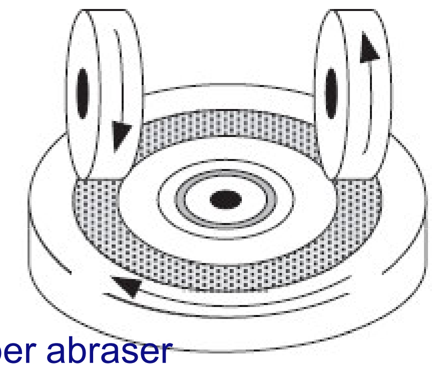
Cutting of a CNT-carbon hybrid composite (Bello et al 2009)



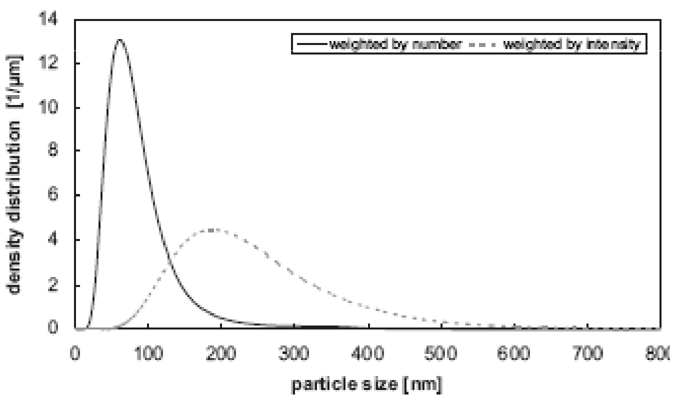


Emission during ('Low energy) machining' of nanoparticles embedded products (2)

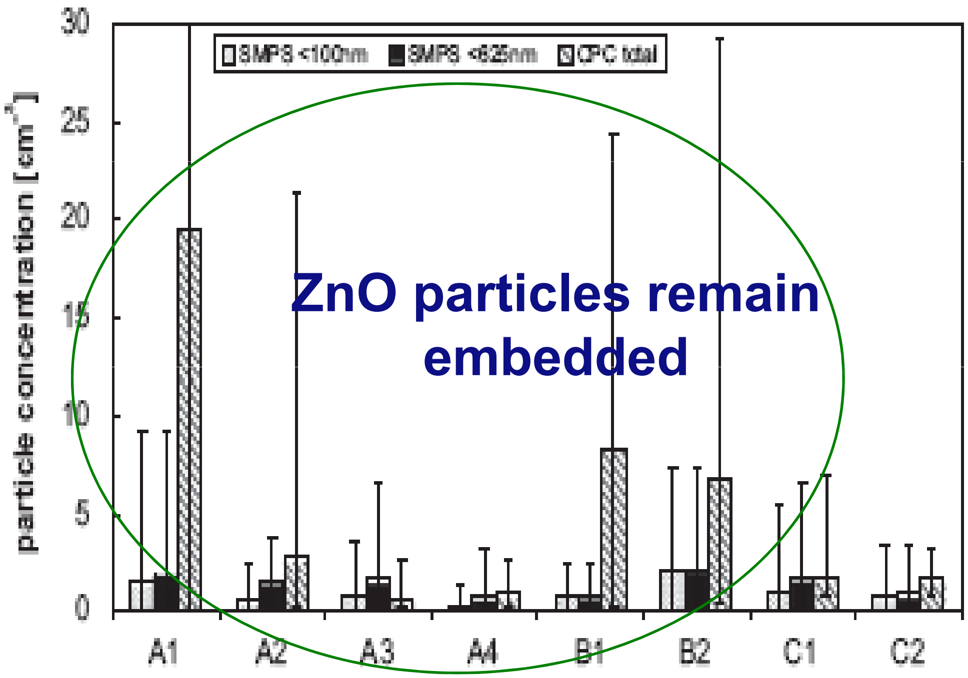
Abrasion induced particle release into air from nano-particle embedded surface coatings (Vorbau et al 2009)



Taber abraser



Particle size distribution of ZnO particles in coating



Particle concentration <100 nm > 100 nm

Observations/ **preliminary** conclusions field studies

manufacturing/downs-stream use/ processing

- Most studies explorative and focused on emssion
- Substantial spatial and temporal variation of (non-MNO?) ‘background’ levels: many other sources
- Outdoor conditions (industrial area/ traffic) and intrusion/ infiltration
- Low ‘contrast’ concentration levels ‘activity’/ handling periods and periods with no/hardly any activity
- Increased particle number concentration: mode particle size distribution > 100 nm (200-300nm) ; increase < 100 nm often associated with combustion and electrical tools
- Characterization; Strong indications for 1) very few primary NPs, 2) many agglomerates, 3) some aggregates
- In general: limited duration of MNO-related activities ≈ exposure duration
- Indications for weak/ hardly any correlation mass/number/surface area
- So far no discrete MN-particles in aerosols released from nanocomposites or end-product

Emission/ workplace air concentration results and personal exposure?

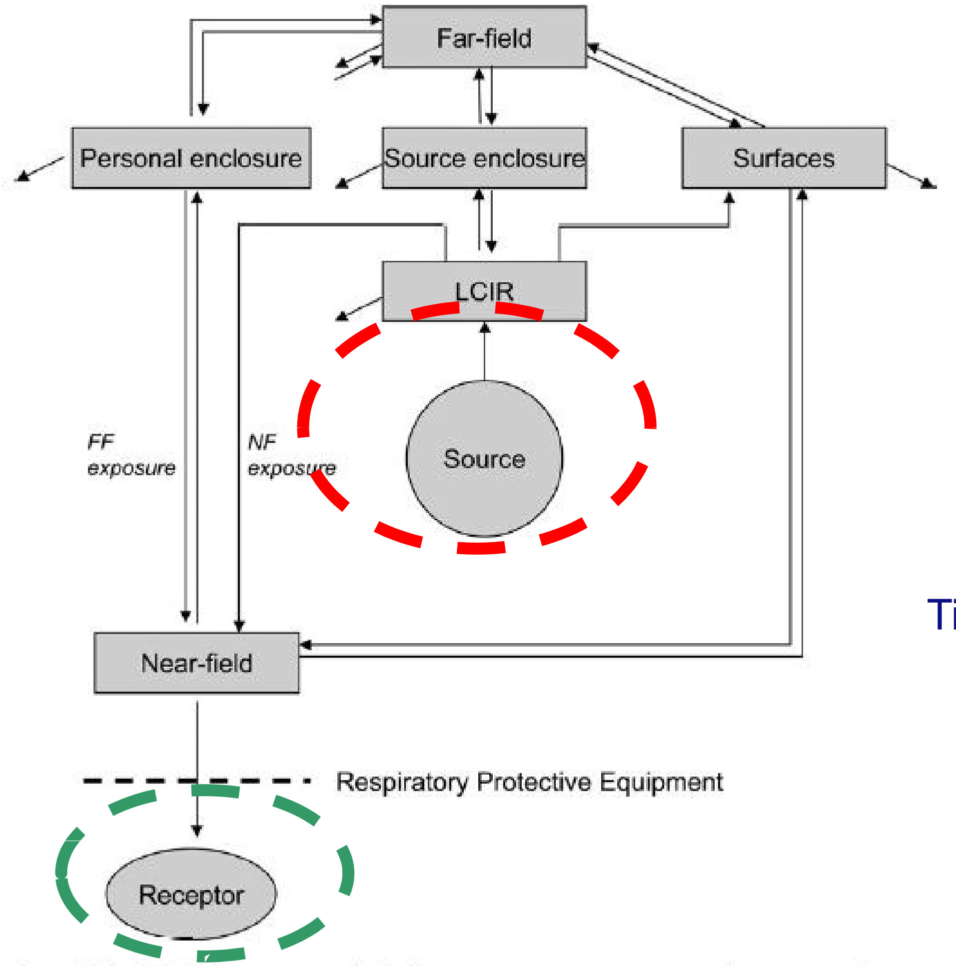
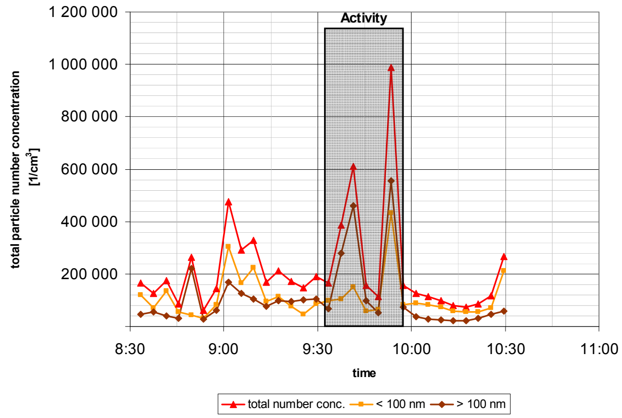
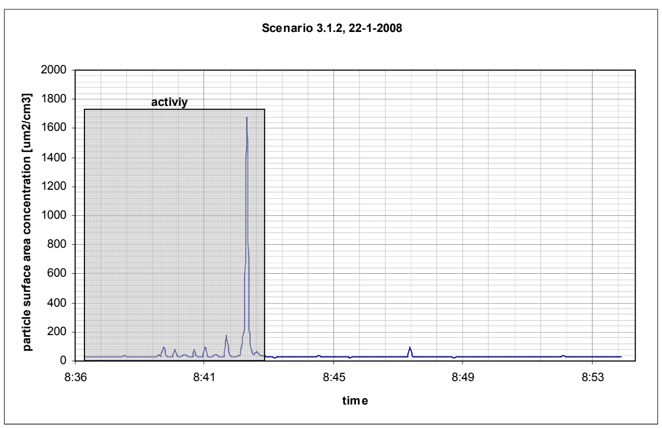


Fig. 1. Conceptual model for inhalation exposure including sources, compartments and receptor and transport between these components.

Tielemans et al 2008

How to get from workstation time/activity- concentration profiles to estimates of personal **Exposure**?





?

Estimate of exposure (per person/shift)	
MNP (fumed silica) Confirmed by TEM analysis	Cumulative MNP surface area(μm2/cm3)
	± 530 (± 2.8%)

Key issues for risk-relevant exposure assessment

- Complex (structured) aggregated/ agglomerated aerosols (no/ hardly any primary Manufactured nano-objects)
  - How easily MNO agglomerates will detach/ de-agglomerate in air / body fluids?
  - What (metric) and how do we measure complex (structured) aggregated/ agglomerated aerosols?
  - How do we distinguish the state of agglomeration of aerosols during measurement or after sampling?
  - New devices for **personal** sampling:
    - miniaturised existing instruments
    - new concepts/ in situ characterization

Decision tree Nano relevance
Precautionary matrix for synthetic Nanomaterials
FOPH/ FOEN Switserland

Flow diagram for the evaluation of nano-relevance:

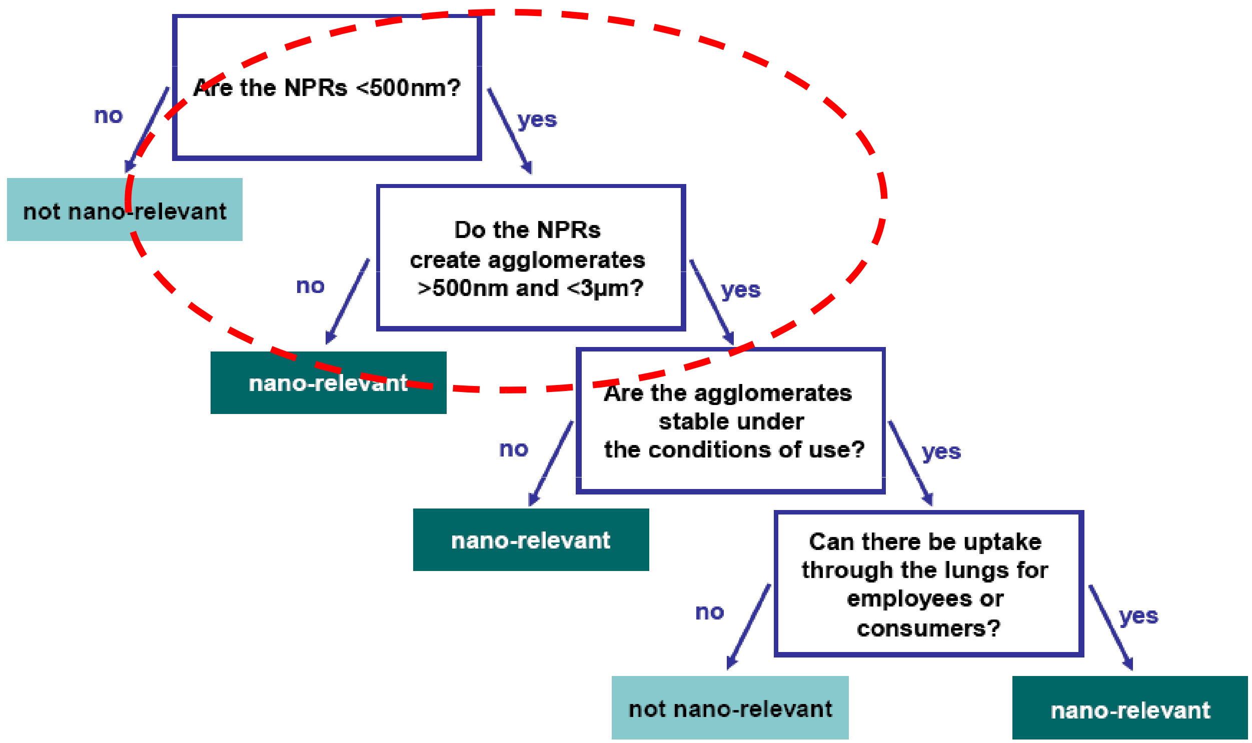


Figure 5: Evaluation of nano-relevance

Key issues for risk-relevant exposure assessment

- Complex (structured) aggregated/ agglomerated aerosols (no/ hardly any primary Manufactured nano-objects)
  - How easily MNO agglomerates will detach/ de-agglomerate in air / body fluids?
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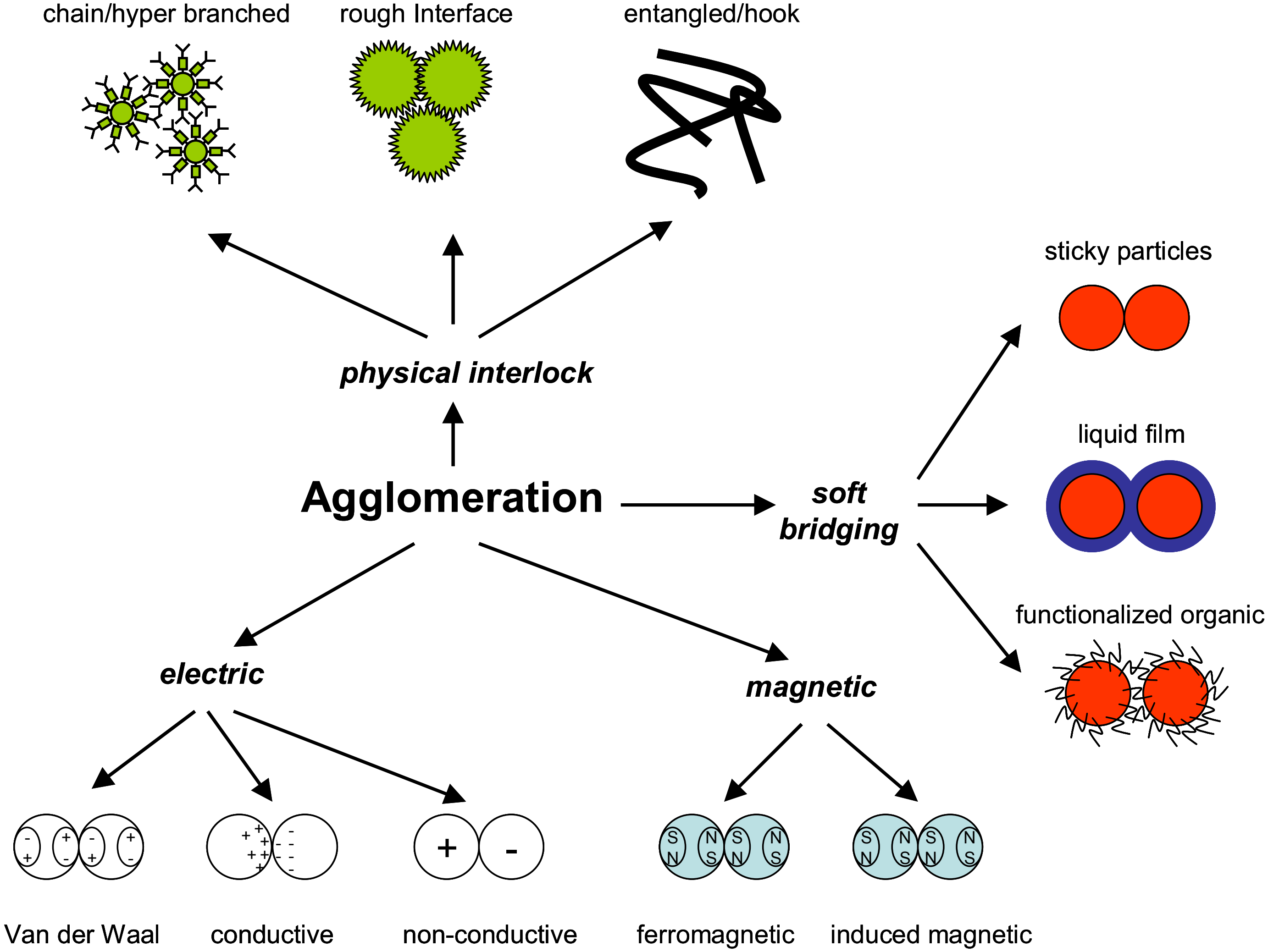
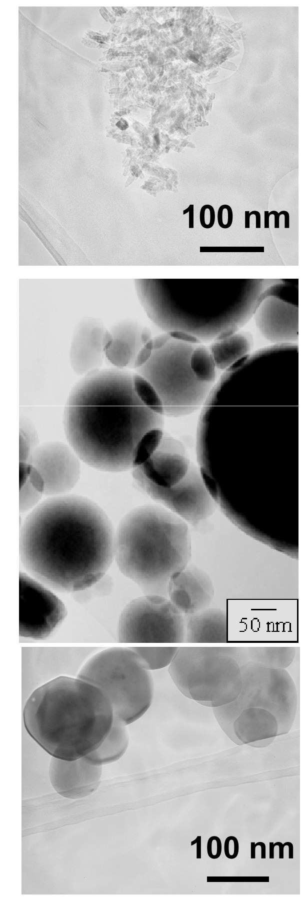
  - New devices for **personal** sampling:
    - miniaturised existing instruments
    - new concepts/ in situ characterization

Powder agglomeration appears inevitable

- could it be more important for Manufactured nano objects/materials?

Adopted from Schneider and Jensen (submitted)





Key issues for (future?) risk-relevant exposure assessment

- Complex (structured) aggregated/ agglomerated aerosols (no/ hardly any primary Manufactured nano-objects)
  - How easily MNO agglomerates will detach/ de-agglomerate in air / body fluids?
  - What (metric) and how do we measure complex (structured) aggregated/ agglomerated aerosols?
  - How do we distinguish the state of agglomeration of aerosols during measurement or after sampling?
  - New devices for **personal** sampling:
    - miniaturised existing instruments
    - new concepts/ in situ characterization
      - Grimm device
      - Philips Aerasense