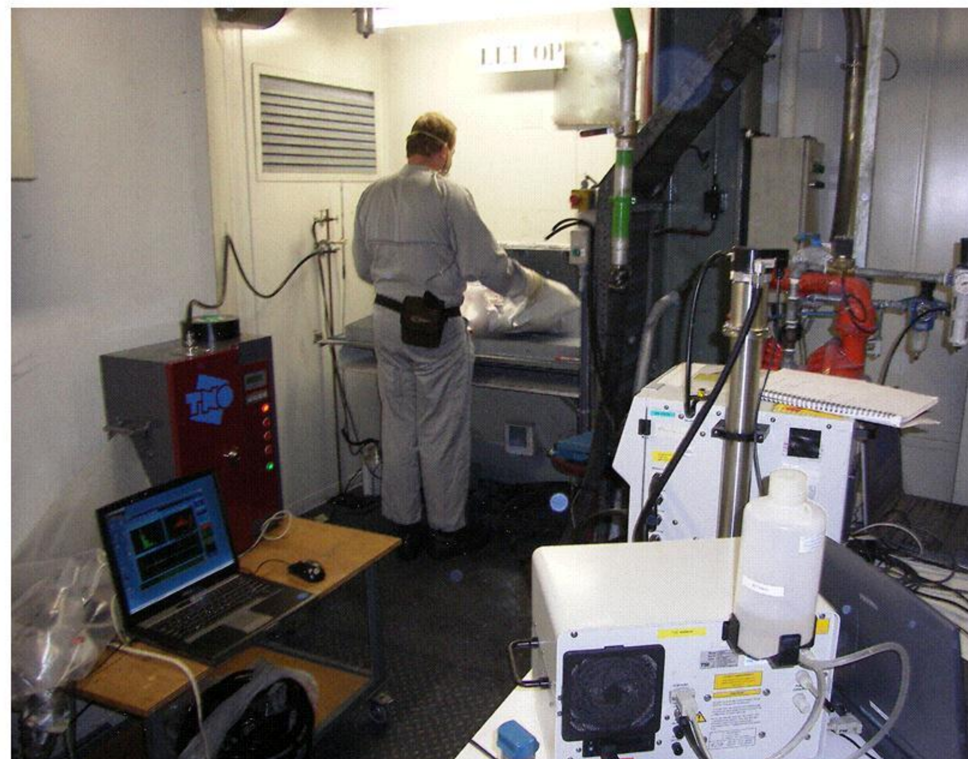
Workplace Air Monitoring Studies

Understanding exposure to manufactured nano objects?

Derk H.Brouwer



Outline

Concepts of Exposure (Models)

Evidence exposure

Preliminary conclusions

Outlook

- development devices
- use of exposure / banding models
- need for data pooling

Fate of aerosols or substances

Emission ***Transmission*** ***Immission***

3. Local controls (*LC*)
4. Dispersion (*D*)
5. Segregation (*Seg*)
6. Surface contamination (*Su*)

Source → Receptor BZ

1. Substance emission potential (*E*)
   - Dustiness
     - particle size (distribution)
     - bonding (agglomeration/aggregation)
     - moistness
     - solidity/intactness/surface modifications/
   - Fugacity
     - (partial) vapor pressure/ diffusion coefficient in air
   - Hardness
2. Activity energy/ emission potential (*H*)
   - Energy transfer/ stress
     - type and level
   - Scale
   - Product-to-air interface

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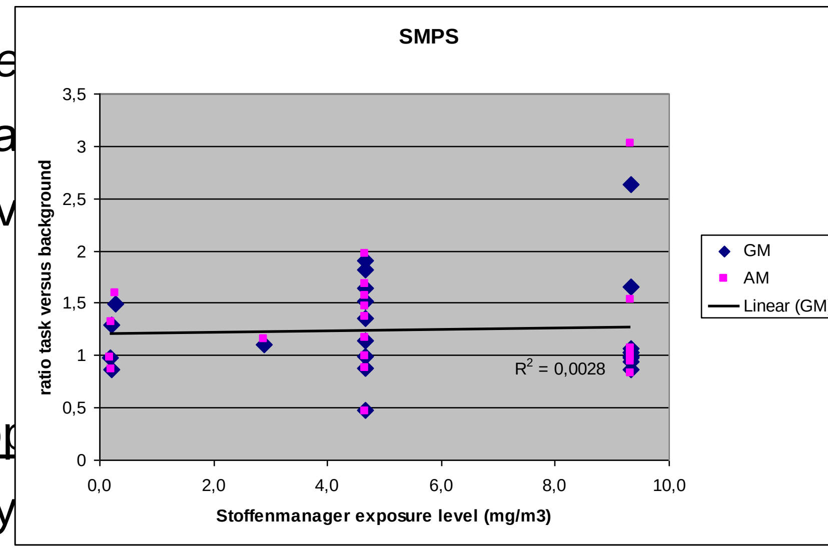
REACH (EU regulations for chemical substances) First Tier Inhalation Model Models suitable for nano?

Comparison of model output with datase

- Basic concepts of models might be a

No correlation could be observ

particle number concentration**



1)scenarios derived data set were not op

resolution of the models could not fully

2) the categories of the model variables are not scaled to nano-materials / calibrated resulting in loss of power of contrast

3) exposure metric **(mass concentration) probably not optimal

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coagulation

Emission *Transmission* *Immission*

3 Local controls (LC)

Journal of Exposure Science and Environmental Epidemiology (2011), 1–14

www.nature.com/jes

Conceptual model for assessment of inhalation exposure to manufactured nanoparticles

T. SCHNEIDER[a,b], D.H. BROUWER[c], I.K. KOPONEN[b], K.A. JENSEN[b], W. FRANSMAN[c], B. VAN DUUREN-STUURMAN[c], M. VAN TONGEREN[d] AND E. TIELEMANS[c]

Mass generation rate [g/min]

Mass concentration [mg/m3]

Additional 'nano features'

Particle size distribution/

number concentration

Particle size distribution/

number concentration

(active) surface area concentration

 

Objectives for (workplace) measurements

process	characterization	
emission	Emission rate	
transmission	Environmental/ workplace concentration	
immission	Micro-environmental/ concentration	
exposure	Exposure concentration,.ie. Size fractionalized/ time-integrated BZ concentration	
intake		Outer exposure surface
	Intake dose	
uptake		Inner exposure surface
	Uptake dose	
Distribution		
Metabolism	Biologically relevant dose	
Excretion	Target dose	

- Potential for emission
- Understanding processes
- Effectiveness of control
- Compliance

- Exposure & Risk assessment
- Epidemiology

Published research papers (2004-present)

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Asbach, et al. (2009). NanoCare Health related aspects of nanomaterials. Chapter 5: Exposure to nanoparticles: measurement, modelling and agglomerate stability	**Maynard, A. D. et al.** (2004). Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material
Bello, D. et al. (2008a). Particle exposure levels during CVD growth and subsequent handling of vertically-aligned carbon nanotube films	**Methner, M.** (2008). Effectiveness of local exhaust ventilation (LEV) in controlling engineered nanomaterial emissions during reactor cleanout operations
Bello, D. et al. (2008b). Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes	**Methner, M. et al.** (2007). Identification and characterization of potential sources of worker exposure to carbon nanofibers during polymer composite laboratory operations.
Brouwer, D., et al. (2009). From workplace air measurement results toward estimates of exposure? Development of a strategy to assess exposure to manufactured nano-objects	**Methner, M. et al.** (2010). Nanoparticle Emission Assessment Technique (NEAT) for the identification and measurement of potential inhalation exposure to engineered nanomaterials--Part B: Results from 12 field studies.
Demou, E. et al. (2008). Exposure to manufactured nanostructured particles in an industrial pilot plant	**Miller, A. et al.** (2010). Characterizing Exposures to Airborne Metals and Nanoparticle Emissions in a Refinery
Evans, D. E. et al. (2010). Aerosol Monitoring during Carbon Nanofiber Production: Mobile Direct-Reading Sampling	**Peters, T. M. et al.** (2009). Airborne monitoring to distinguish engineered nanomaterials from incidental particles for environmental health and safety
Fujitani, Y. et al. (2008). Measurement of the physical properties of aerosols in a fullerene factory for inhalation exposure assessment	**Tsai, S.-J. et al.** (2008a). Airborne nanoparticle release associated with the compounding of nanocomposites using nanoalumina as fillers
Han, J. et al. (2008). Monitoring multiwalled carbon nanotube exposure in carbon nanotube research facility	**Tsai, S.-J. et al.** (2008b). Airborne nanoparticle exposure Associated with the manual handling of nanoalumina and nanosilver in fume hoods
Kuhlbusch, T. A., et al. (2004). Number size distribution, mass concentration, and particle composition of PM1, PM2.5, and PM10 in bag filling areas of carbon black production	**Yeganeh, B. et al.** (2008). Characterization of airborne particles during production of carbonaceous nanomaterials
Kuhlbusch, T. A. J., and Fissan, H. (2006). Particle Characteristics in the reactor and pelletizing areas of carbon black production	**Koponen IK et al** (2010) Comparison of dust released from sanding conventional and nanoparticle-doped wall and wood coatings

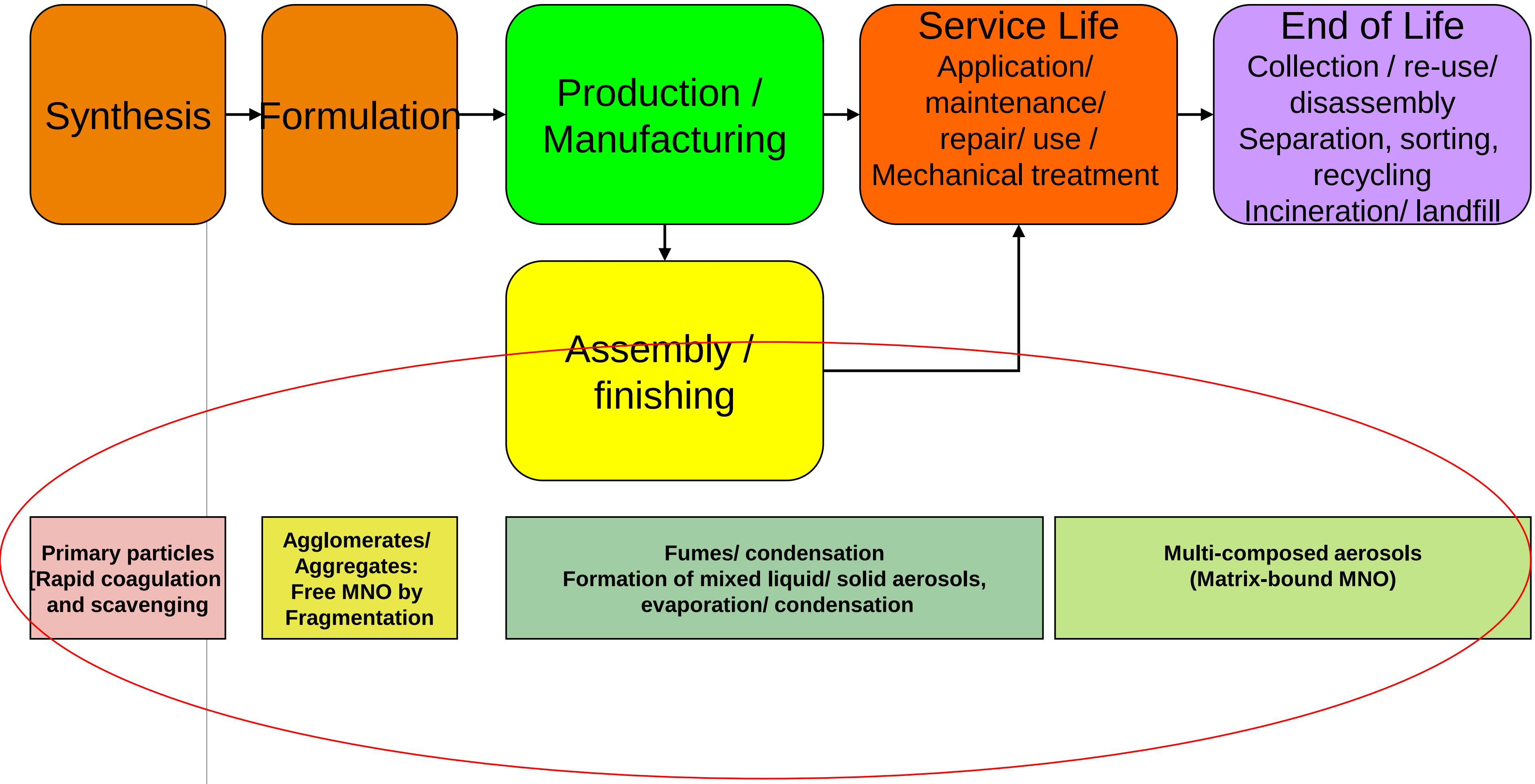
≈> 40 publications

≈ 40 % 'real workplace'

≈ 60% experimental/workplace simulations

≈ 30 % focussed on EA/RA

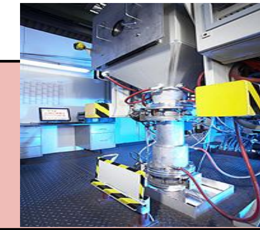
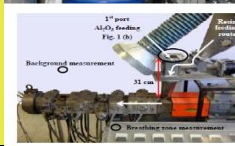
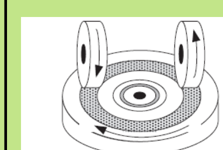
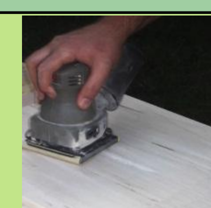
≈ 70% focussed on exposure analysis, emission, control etc


Synthesis
Formulation
Production / Manufacturing
Service Life
Application/ maintenance/ repair/ use / Mechanical treatment
End of Life
Collection / re-use/ disassembly Separation, sorting, recycling Incineration/ landfill
Assembly / finishing
Primary particles [Rapid coagulation and scavenging
Agglomerates/ Aggregates: Free MNO by Fragmentation
Fumes/ condensation
Formation of mixed liquid/ solid aerosols, evaporation/ condensation
Multi-composed aerosols (Matrix-bound MNO)

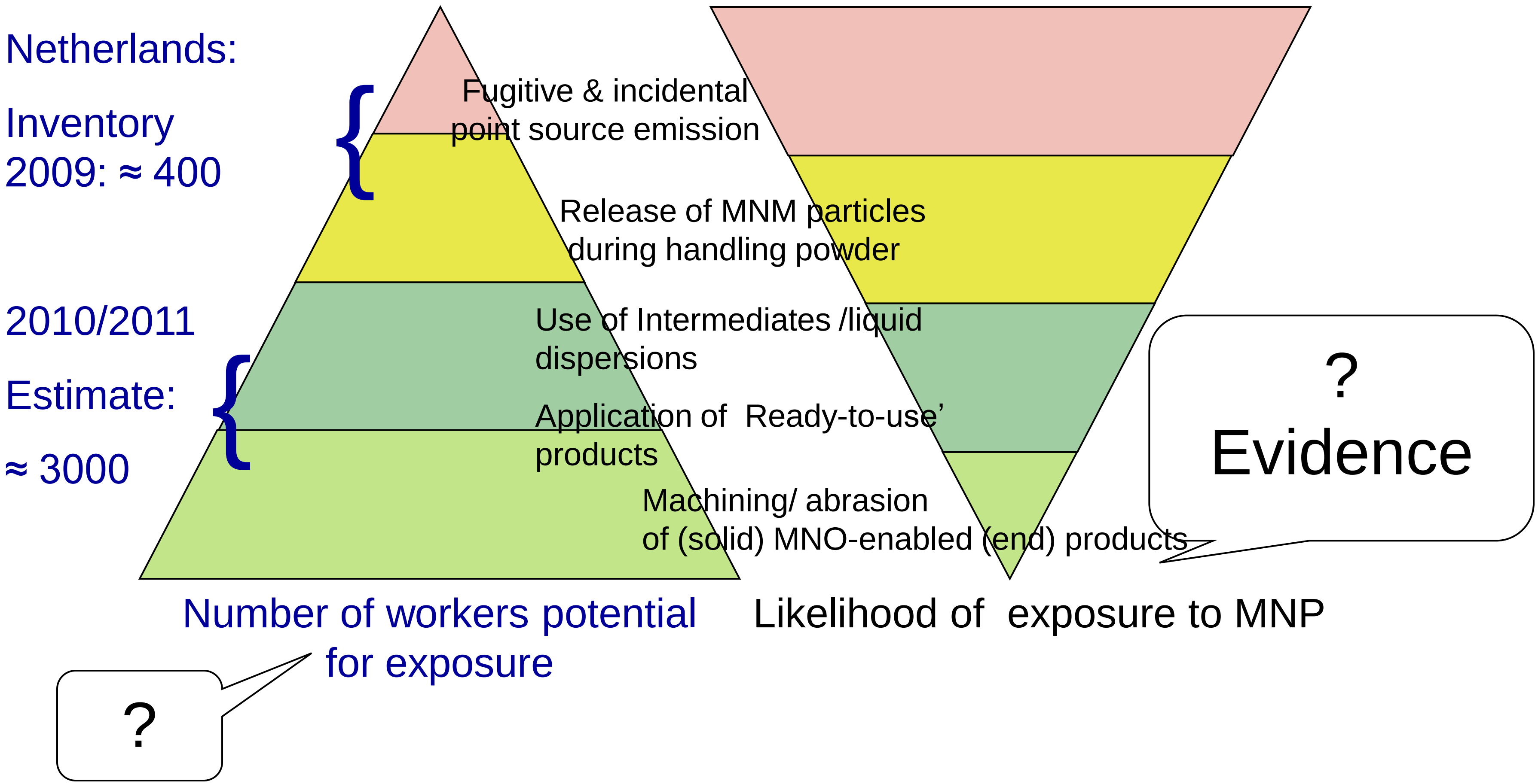
Examples of Nanomaterial generations

First Generation/ passive Nanomaterials	Second generation/ Active Nanomaterials	Third- and Fourth Generation/ NanoSystems
Additives to solid matrices to improve physical properties	Functionalized: e.g nanoAg, nanoAu, dendrimes (diagnostics/ therapeutics)	Integrated / molecular nanosystems e.g. multi-functional nanomedicines
Carbon Black nanoTiO2 nanoSiO2 Carbon Nanotubes	Nanoscale active components of integrated circuits e.g. functionalized CNT, graphene	Atomic devices ‘designed ’by human

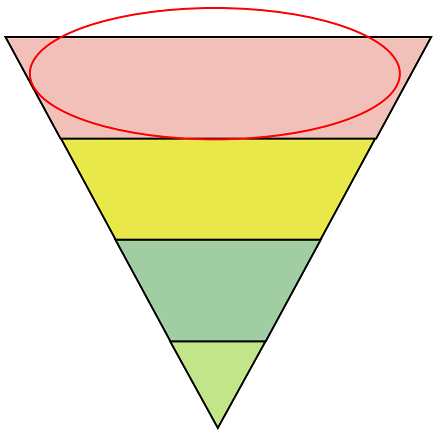

‘Nano- specific’ Emission generation domains Schneider et al 2011

Source domain	Examples	
Fugitive & incidental point source emission during MNO **synthesis**	Leaks through connections, seals etc during MNO synthesis/ incidental release	
Release of MNO particles during **handling**/ transfer of MNO **powder**/ bulk material	Bagging/ bag dumping Weighing Dispersion/ compounding in composites	 
Intermediates master batch/ granules liquid dispersions **Ready-to-use’ products**	Pouring/ injection moulding Pouring/ stirring/ mixing Nanofilm sprays dispenser Nano coatings	 
Machining/ abrasion of (solid) MNO-enabled (end) products/ End of Life (EoL)	Low (abrasion) energy High energy (sanding/ grinding, cutting) High temperatures	 

Assumptions exposure to Manufactured Nano Objects
(MNO) (spheres, tubes, fibers)

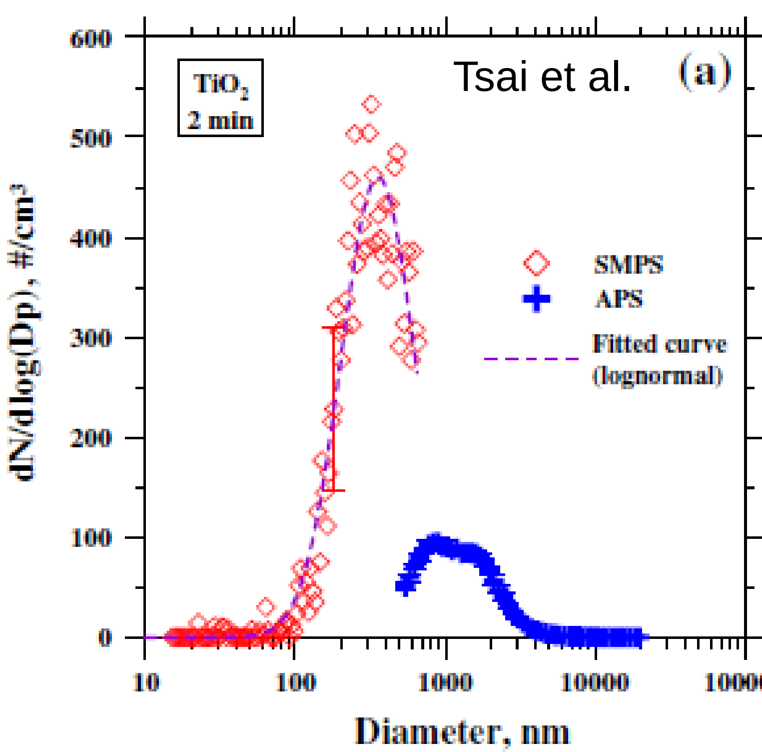


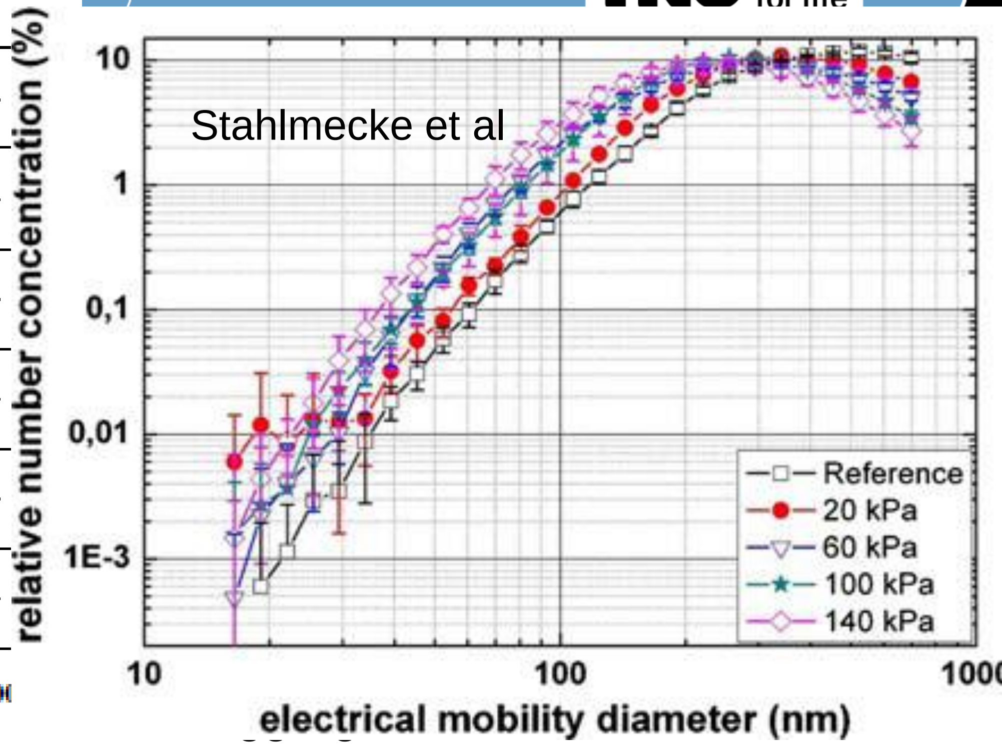
Evidence likelihood: emission during synthesis



- (Simulated) workplace studies, e.g. Demou et al 2008,2009, Methner et al. 2009, 2010,Tsai et al, 2008, Asbach et al 2012 etc
  - emission of MNO is likely
  - process and characteristics determine size and concentration
  - Enclosure/RMM effective

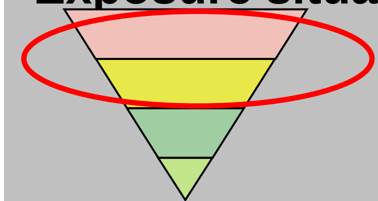
- Experimental studies & modeling
  - Rapid coagulation (concentration > 10^6 particles/ cm^3)
  - Scavenging (attachment to (larger) BG aerosols)



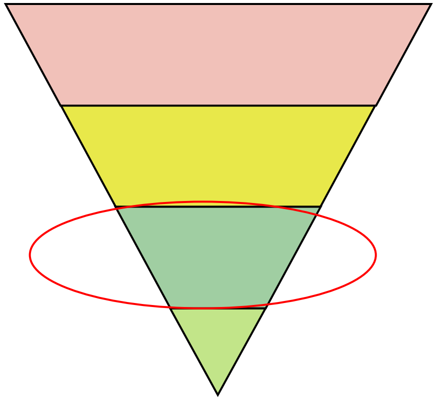


- Studies Dustiness & Fractioning e.g Schneider & Jensen 2008, Jensen et al. 2008, Schneider & Jensen 2009; Tsai et al. 2009;. 2009; Seipenbush et al. 2009
- (few) Particles < 100 nm can be generated (size mode ≈ 200-300nm) ; mostly agglomerates
- Fragmentation: High shear forces needed

Overview of distributions of likelihood of exposure to MNO as function of workplace exposure scenario (EU-NANOSH)

	Distribution “likelihood of exposure		
Exposure situation 	**“not likely” (n)**	**“possibly/ not excluded (n)**	**“likely“ (n)**
Production – commercial (n=20)	9	11	0
Production – non commercial (n=5)	2	3	0
Down-stream-use – commercial (n=17)	11	6	0
Down-stream-use – non commercial (n=12)	8	3	1
Total (N=54) (Fully characterized)	*30 (56%)*	*23 (42%)*	*1 (2%)*

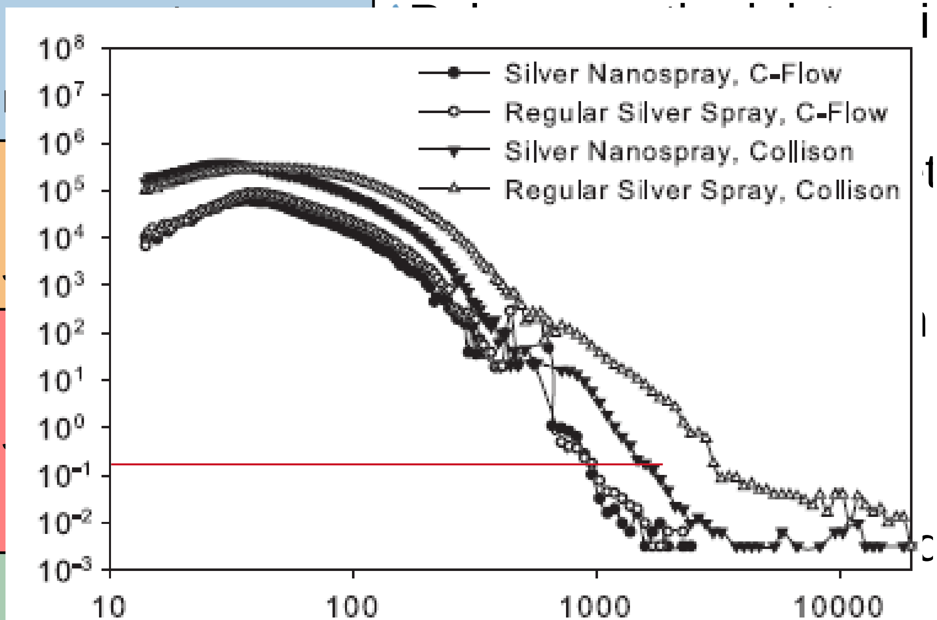
Evidence likelihood: emission during application of ‘ready-to-use’products e.g. ‘nano’ sprays

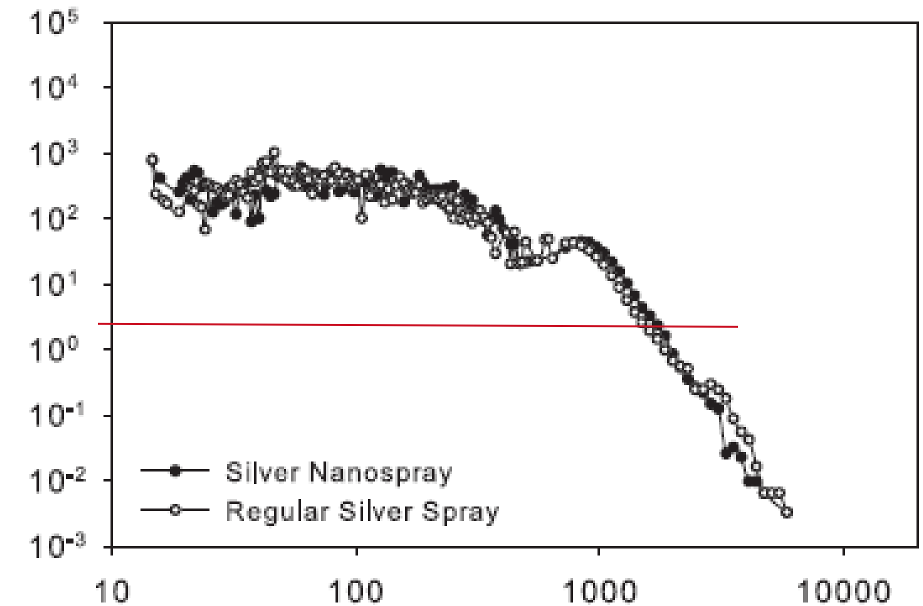


- Experimental studies & simulations

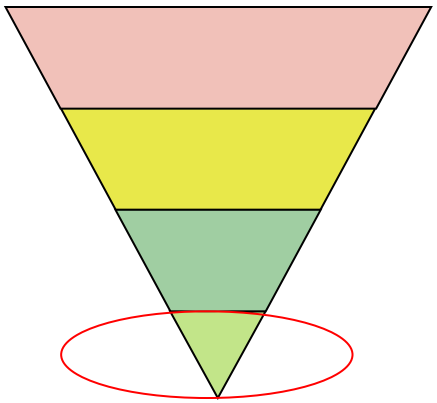
Study	Spray		Release			Room	Sampling
	N	type	method	amount (g)	time (s)	(m3)	position
Nørgaard et al Environ Sci Tech 2009	4	alcohol -based	Pump (HH) Gas container	8 -13.6	25 max	0.66	NF
Hagendorfer et al J NanoPart Res 2010	1	water based	Pump (HH) Gas container	0.68	1	0.33	Exhaust air
Lorzenz et al J NanoPart Res 2011	4	various	Gas container Pump (HH)	0.2-3.5	1-5	0.33	Exhaust air
Nazarenko et al JESEE 2011	11	various	Pump (HH) Nebulizers	?	180max		BZ
Chen et al (2010)	1	?	Gas container	?	150max	?	BZ
Bekkers et al In preparation	4	alcohol -based	Gas container	6.1 – 11.9	3 x 3	19.5	NF/FF
Quadros & Marr 2012)	3	water	Gas container		1800	0.52	Exhaust air

Study	Released aerosols	Evidence of MNO
JESEE 2011	›No indication that presence of MNO in spray solution affects size distribution ›Aerosol composition differ from liquid	
Chen et al Inhal Tox 2010		nanoparticles detected (nanoTiO2)
Bekkers et al		nanoparticles detected (antiperspirant Al, Mg)



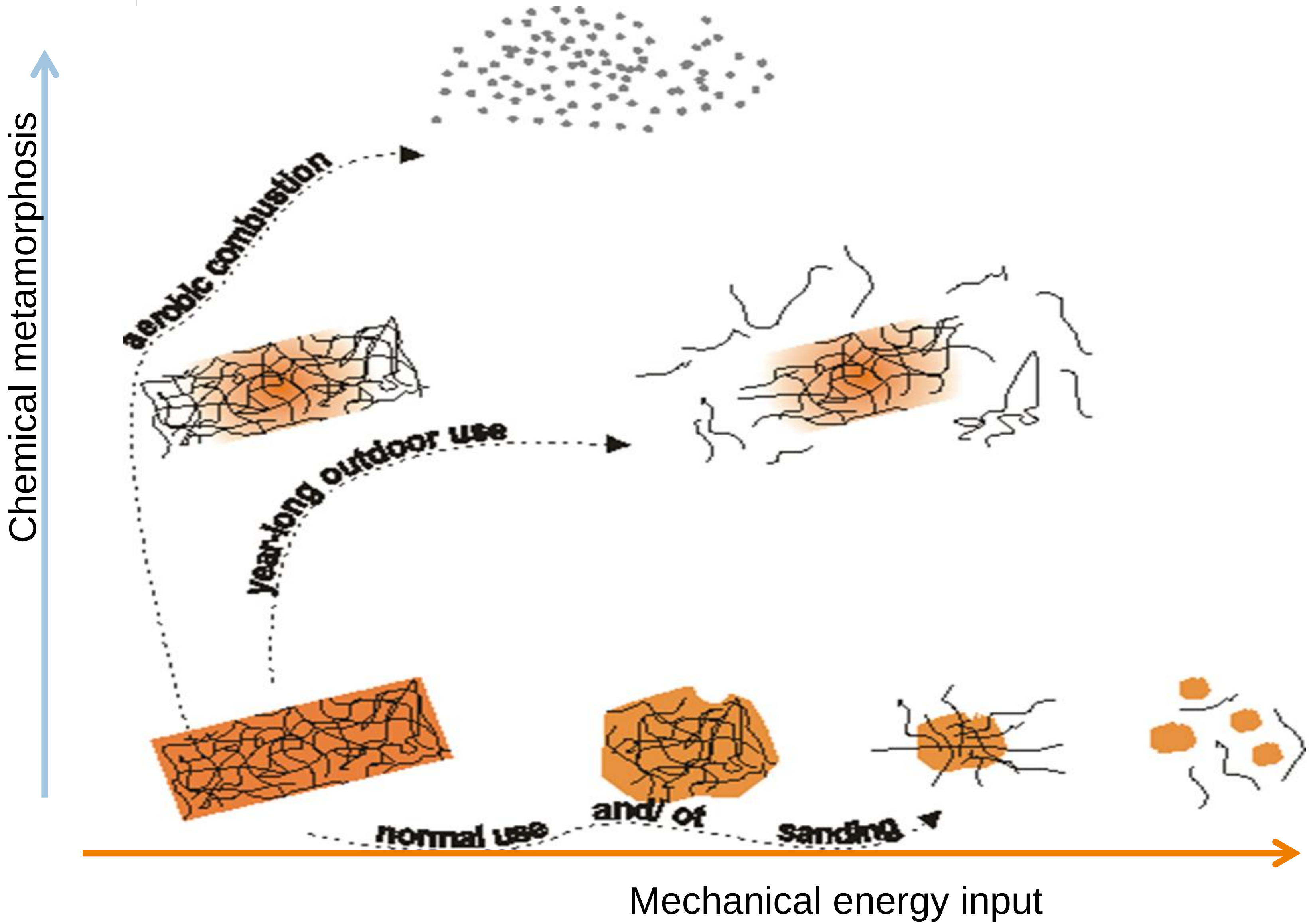


Evidence likelihood: emission during machining (abrasion) of nano-composites or nano’end’products (and EoL activities)



- Experimental & simulation studies
- Coated surfaces
- Composites (Nana materials embedded in a polymer matrix)

Degradation intermediates (source Wohlleben 2012)



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	Energy		Operation	Study	Substances
	L	H			
Nano coating	Δ		wear	Vorbau et al 2009	ZnO doped coatings
		Δ	sanding	Koponen et al 2010	Various types of paints and lacquers with different MNO
				Göhler et al. 2010	PU coating & architectural coating: MNO ZnO,Fe2O3

Conclusions from low energy abrasion studies

- Standardized stress (TABER)
- Release of nano-size particles is observed
- Low particle concentration
- Effect of nanofiller can be observed

Guiot et al)

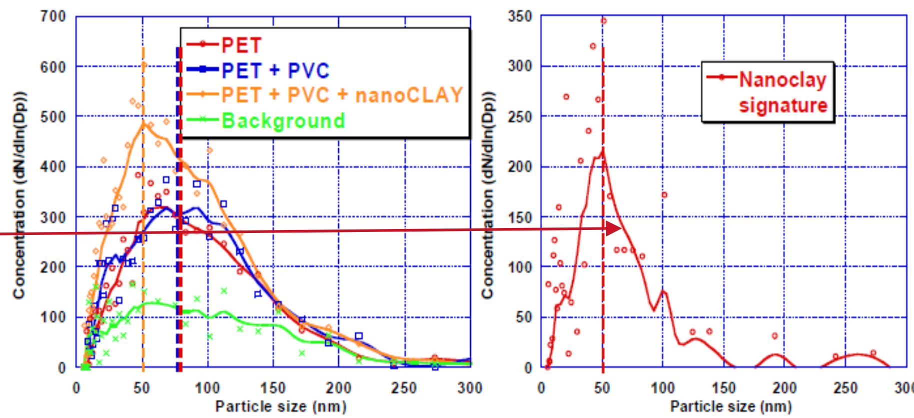
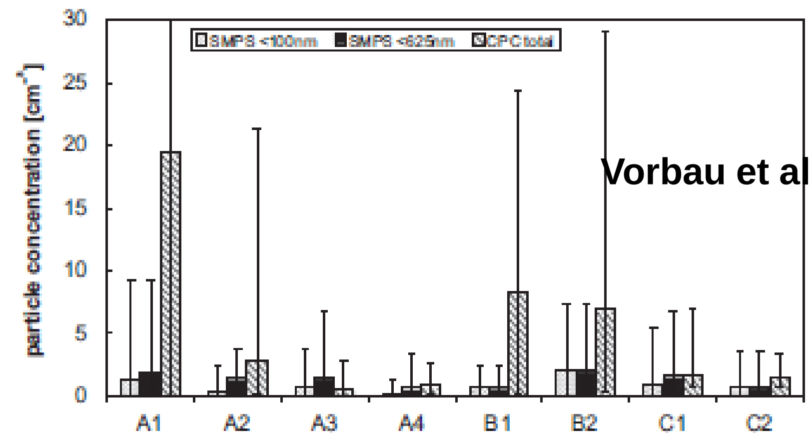


Figure 4. Abrasion test results obtained on a fabric constituted of a PET layer coated with a PVC coating containing or not nanoclays.

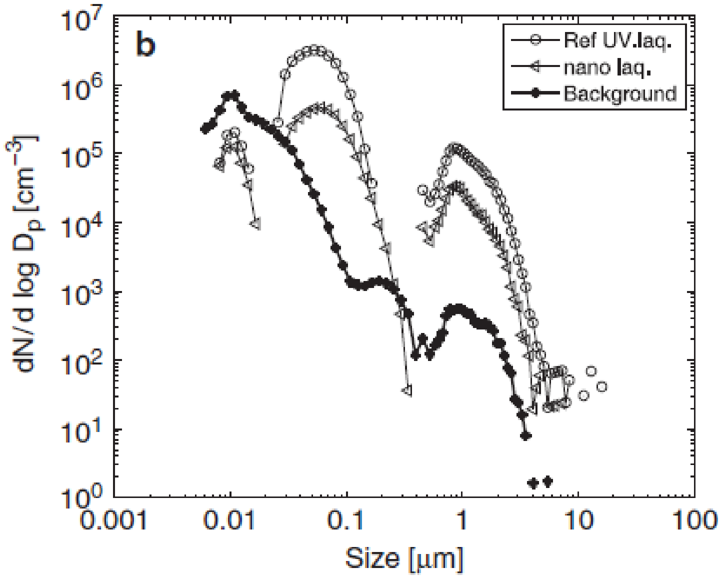
- The released particle mass depends on substrate and coating but there is no significant correlation to nanoparticle content
- the zinc oxide particles are still embedded in matrix




Conclusions from nano coating sanding studies

(Koponen et al 2010;Gohler et al 2010)

- In general size of release aerosols determined by input energy/stress, sander paper grain size etc
- Particle number (and size) concentration depends on type of coating e.g. PU, wall-architectural etc.
- No significant differences between MNO containing coatings and ‘conventional’ coatings
- Effect of hardness not yet clear
- Strong indication composition aerosols similar to matrix materials, i.e. NMO are embedded

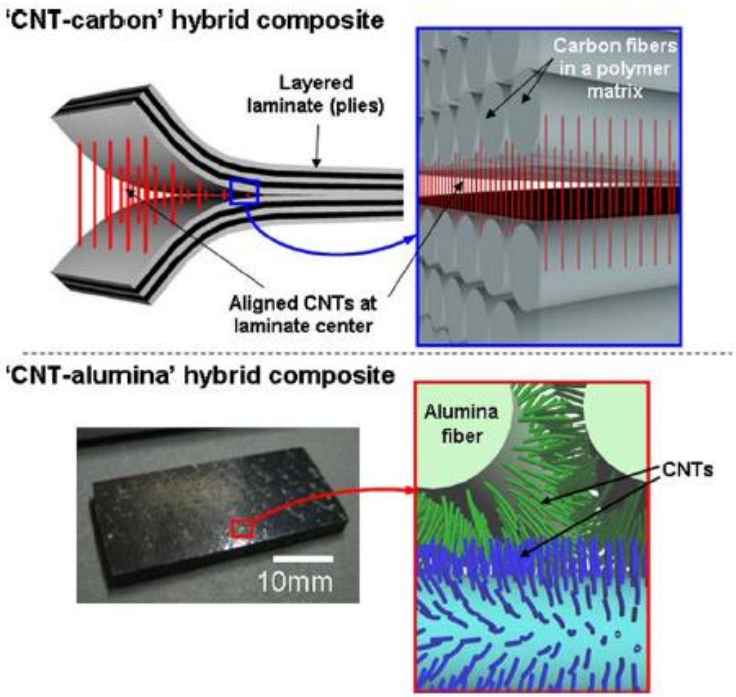


	Energy		Operation	Study	Substances
	L	H			
Nano-	Δ		wear	Guiot et al 2009	PET coated with PVC with nanoclay filler
composites		Δ	cutting-sawing	Bello et al 2009	Base- & CNT alumina
		Δ	drilling	Bello et al 2010	Base- & CNT carbon
	Δ		wear	Wohlleben et al 2011	PA + SiO2 POM + CNT Cement + CNT
		Δ	sanding	Wohlleben et al 2011	PA + SiO2 POM + CNT Cement + CNT

Conclusions from composites – machining studies

(Bello et al, 2009, 2010)

- Higher input energies , e.g. (drilling/ cutting) speed, higher process time associated with thickness result in higher particle concentration.
- Dry (cutting/ drilling) >>> wet
- Type of composite affects size distribution (not necessarily caused by CNT).
- Cutting: no free CNTs, bundles , or aggregates, CNT at fractured surface
- Drilling: aggregates of CNTs, higher temperatures: smoke, decomposition



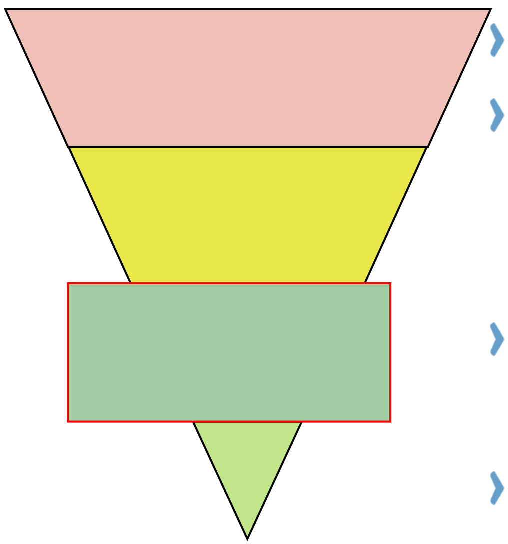
Preliminary conclusions source generation domains

Source	Emission	Breathing zone
Fu  oint source er synthesis	Primary particles/objects; [Rapid coagulation and scavenging]	Discrete/ detached MNO (likely)
R  cles during ha NO powder/ bu	Agglomerates/ Aggregates: Fragmentation	Discrete/ / detached MNO (not unlikely)
Intermediates m  ules lic 'Ready-to-use' products	Fumes/ condensation Formation of mixed liquid/ solid aerosols, evaporation/ condensation	Discrete/ / detached MNO (not unlikely)
Machining o  roducts containing e O	Multi-composed aerosols	Discrete/ detached MNO (unlikely(?))


Summary observations/ preliminary conclusions

Likelihood of exposure

!?



End of Life ??

- Large variation of exposure scenarios (from Synthesis to End of Life (EoL)) Only a few scenarios has been (appropriately) measured & characterized.
- Source domains 1& 2 : Evidence for exposure
- Source domain 3: Indication for exposure
- Source domain 4: (including EoL): Few data for unambiguous evidence likelihood of potential for exposure.
- Exposure data will remain scarce in future
  - Need for exposure scenario building & modeling :
- Quantification of exposure next step
  - Instrumentation (measure/ analyze)
    - personal AND MNO specificity & repeated sampling
- Uncertainty risk assessment

Promising approaches and developments measurement& risk management

- Measurement devices and characterization

- Exposure Modeling
  - Use for Control (Risk) Banding
  - Initiatives for Harmonized Measurement strategy & data pooling

Promising developments: New devices/ monitoring concepts (1)

‘Nano specific’ exposure issues	Current drawback	Developments
Coagulation processes / interaction with background aerosols occur during transport to worker after emission	No device/ samplers for Breathing Zone concentration	-Variety of new personal samplers/ monitors and portable sensors -Modelling of coagulation/ interaction processes for workplace scenarios
No agreement on (health-) relevant exposure/ dose metric	Suite of devices needed to address all exposure metric	-Integrated/ modular system to monitor particle concentration, surface area concentration + sampling - Surface area concentration screening device

‘Nano specific’ exposure issues	Current drawback	Developments
Identification of MN-objects key factor for background distinction	MNO-specific monitors lacking Sampling + off-line analysis (chemical/ EM) needed	-Specific monitors e.g. for nano-fibers -Size-selective (pre-selection-multi-stage) samplers Detection system (/ sensors) for deposited particles Quantification of TEM analysis
Gap between exposure monitoring and health-effects	(health-) relevant exposure assessment methods are lacking	-Modification of (personal) sampler for cell exposure -catalytic and surface-chemical aerosol monitoring

Basics Control Banding Tools

- Qualitative risk assessment in context of uncertainty
- Risk paradigm
  - R= f { (**hazard**/ severity), (**exposure**/probability)}

Precautionary principle

- Uncertainties: conservative approach **risk**: → minimize exposure

Risk/Control Banding

- **Hazard** (severity) and **Exposure** (probability) bands linked (not quantitatively) to **Risk** Bands
- **Risk** bands linked to Level of Control
  - CL 1 (Ventilation)
  - CL 2 a/b (LEV/ fume hood)
  - CL 3 (Containment)
  - CL 4a/b (Full containment/ review by specialist)

Note: Exposure models include control measures in exposure estimates!

Risk Level Matrix (Example)

HAZARD BANDS / EXPOSURE BANDS	A	B	C	D	E
1	3	3	3	2	1
2	3	3	2	2	1
3	3	2	2	1	1
4	2	1	1	1	1

In CB tools are Risk levels associated with recommended Level of Control

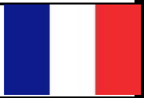
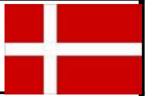
Currently available Risk Prioritization(Evaluation)/ CB tools

	Precautionary Matrix	Risk Prioritization	Web-available spreadsheet www.nanotechnologie.admin.ch
	NanoCB tool (Paik & Zalk 2009)	Control Banding	Table/published paper
	ANSES NanoCB tool	Control Banding	(Web-available) Report www.anses.fr
	Stoffenmanager Nano 1.0	Risk Prioritization	Web-based tool http://nano.stoffenmanager.nl/
	NanoSafer	Risk Evaluation (semi- quantitative)	Web-based tool http://nanosafer.i-bar.dk/

Validity domains

Emission *Transmission* *Immission*

Source → Receptor

	Emission Potential			Immission/ exposure	
	CONTROL BANDING			RISK BANDING	
Source Domain					
Synthesis	(☺)	☻		☻	
Powder Handling	(☺)	☻	☻	☻	☻ ☻
Ready-to-use products	(☺)		☻	☻	
Machining/ abrasion	(☺)			☺	

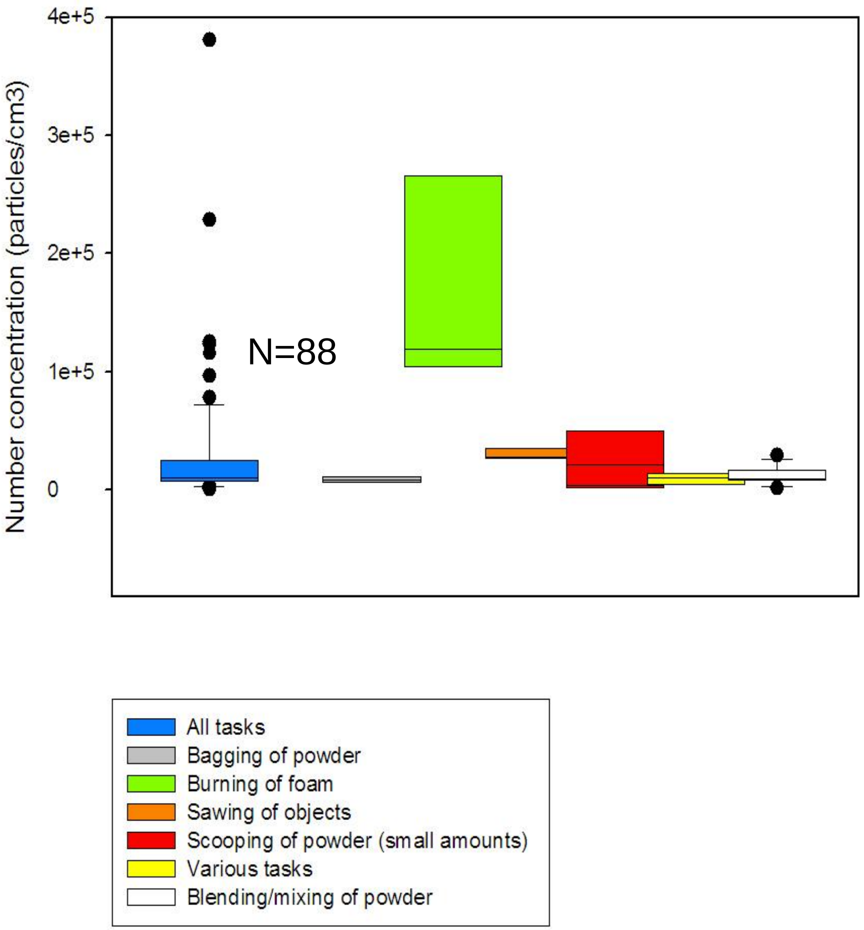
Developments Exposure models

- Pooling of (future) exposure data needed:
  - Harmonization of measurement strategy etc
  - International ("global") Workshops 2010 Irl; NL; 2011`: USA
  - DATAbase Initiative in EU – linkage to US initiative is aimed
  - National programs Measurement/ Campaigns (e.g. Germany, Netherlands, France, USA, …Japan?..etc should populate database
    - Database should enable
      - scenario building
      - meta analysis
      - model calibration & validation

Detailed data analysis: examples NANOSH data set

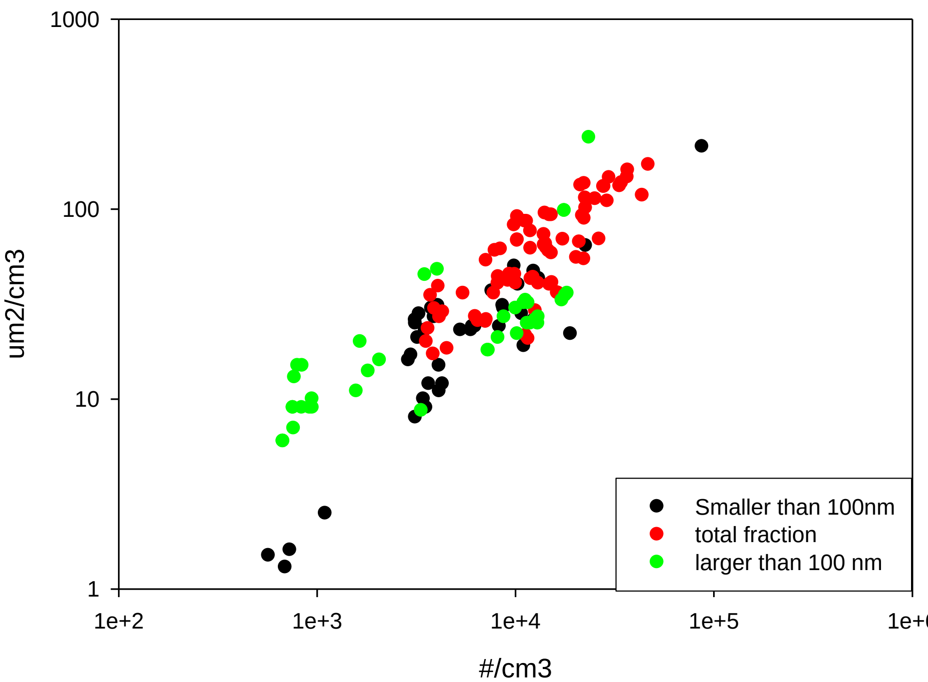
TASK-based particle number concentration

SMPS, particles smaller than 100 nm



Correlation (DC- measured) surface area concentration-

particle number concentration

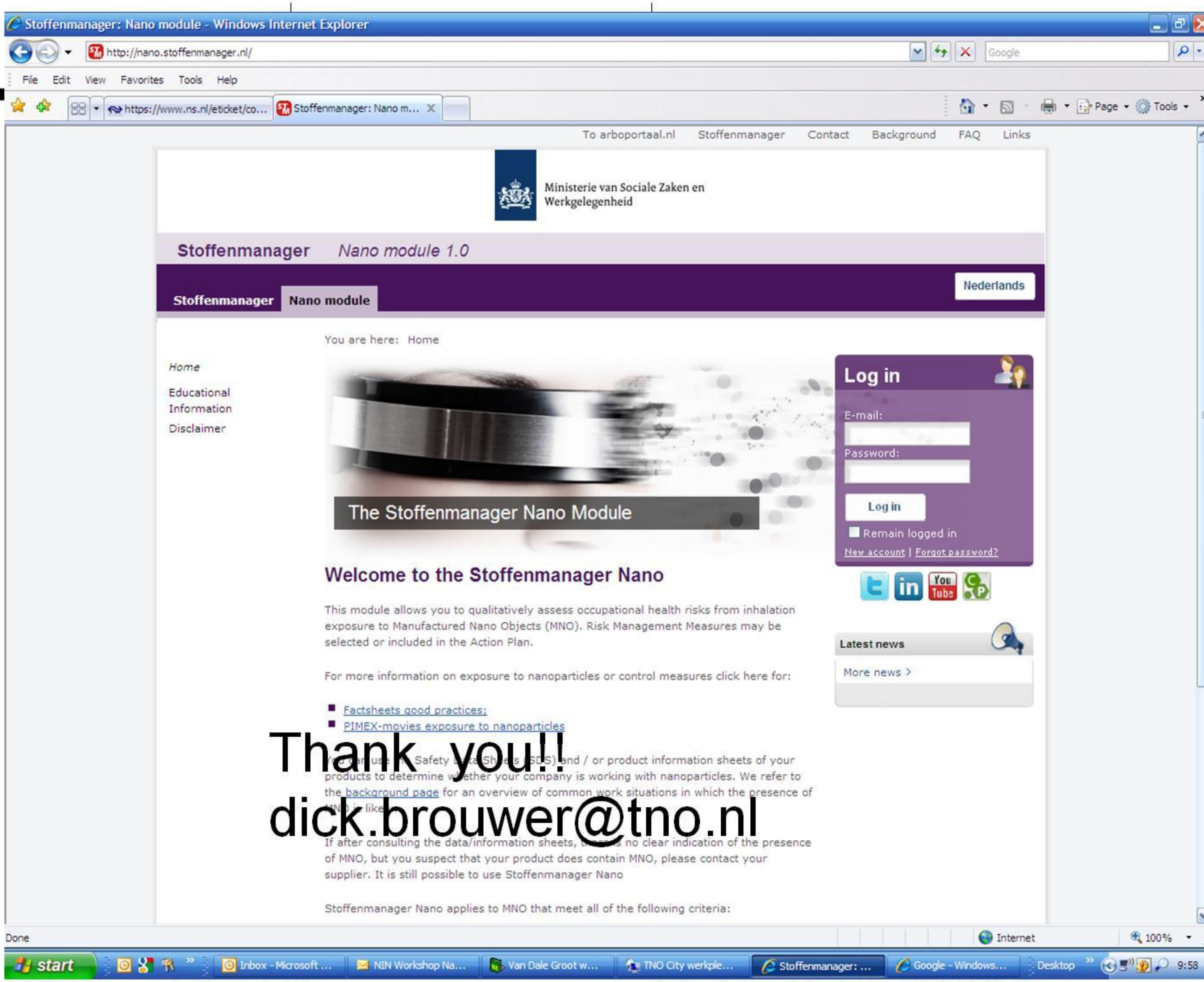


NSAM A	n=40
LQ 1	n=74
NSAM T	n=39

Summary

- Many exposure scenarios with potential for exposure; only a few have been characterized
- Combination of increasing number of studies AND a systematic approach e.g. conceptual model, brings more knowledge about process of exposure
- Quantification of exposure (and risk) currently not possible (instrumentation/ characterization, metric, evaluation criteria)
  - Promising developments Instrumentation
  - Qualitative risk prioritization/ control banding tools

- Urgent need for data pooling
  - Ongoing initiatives
    - Harmonization of data collection, analysis and reporting
    - Data base structure



Thank you!!

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