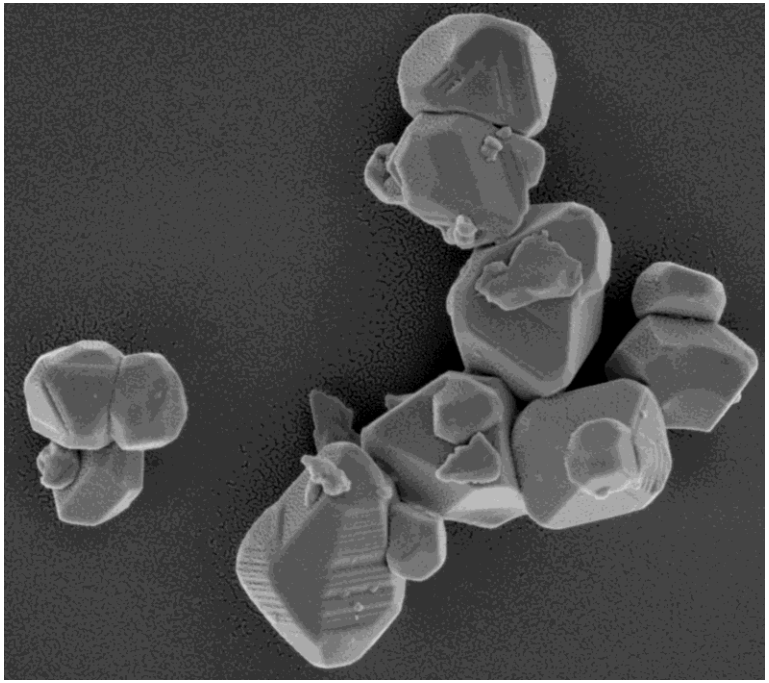
Risk assessment of occupational used nanomaterials

Polder- en niet-poldermodellen vergeleken



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17th of April 2013

Risk assessment of occupational used nanomaterials

A comparison of risk assessment methods in order to determine the risk of occupational used nanomaterials in a research environment

Polder- en niet-poldermodellen vergeleken

Introduction

Nanomaterials and properties
Risk assessment in general

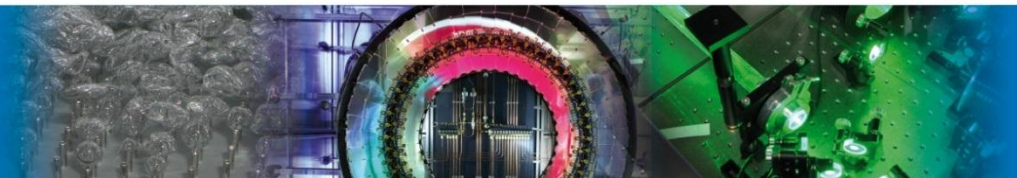
Aim of the study

Results

Inventory
Theoretical comparison (criteria analysis)
Field study

Conclusions

Recommendations



Nanomaterials and properties

Definition used in the study:

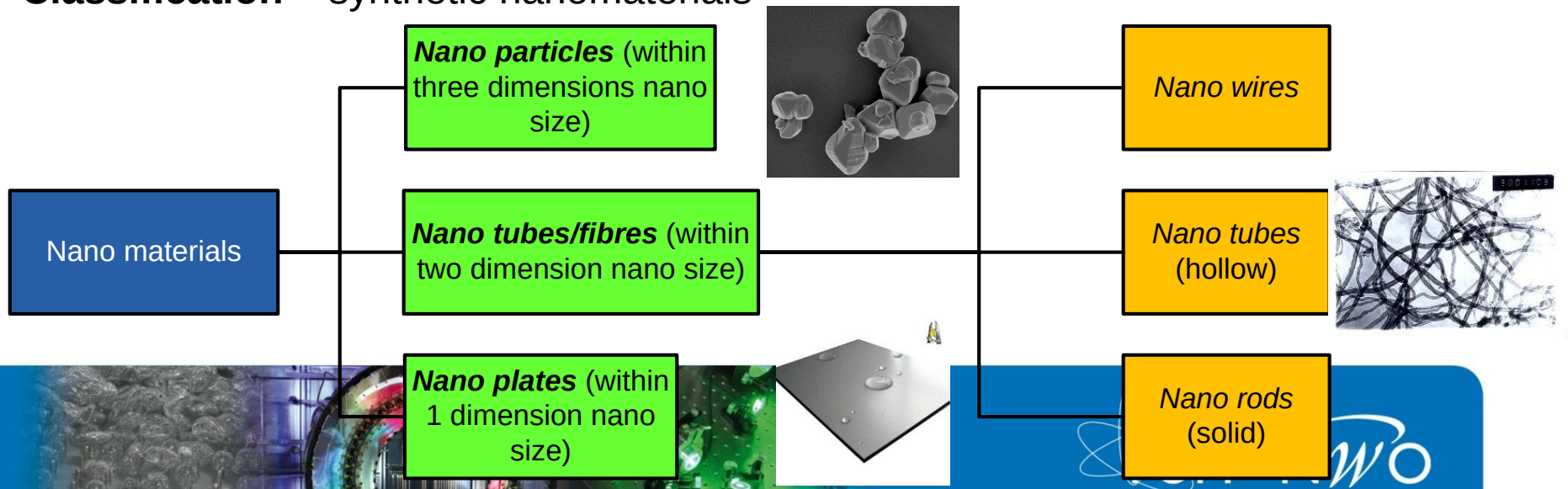
Engineered Nano Particles (ENPs) – Nanomaterials intentionally made by humans

Dimensions: one or several dimensions within the range of 1 – 100 nm

Classification – all nanomaterials

Origin		
Natural	(e.g. ashes from volcanoes)	
Man-made	Unintentional	Intentional
	Products during certain processes (i.e. manganese nanoparticle during welding and emission of nano carbon particles during combustion)	Synthetic nanomaterials (production of nano carbon tubes and TiO_2 within nano size)

Classification – synthetic nanomaterials



Nanomaterials and properties

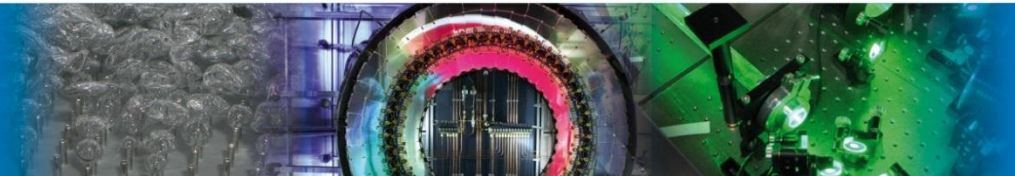
Properties of ENPs:
Dimension (size)
Shape
Chemical composition (including health-related properties)
Surface (dimension & chemical composition)
Solubility

Exposure and health effects

Main exposure routes: Via respiratory system (lungs) and skin (dermal)
Health effects: Inflammation, cytotoxic, fibrosis, asbestos-like symptoms

Properties of a research enviroment

-Small amounts (µg to a kg)
-Large variety
-Continuous changing processes
-Well equipped labs
-Highly educated employees
-Development of new ENPs or moderate ENPs



Risk assessment in general

Risk assessment consists of three parts:

#	Approach	STOP
1a	Elimination	S
1b	Substitution and reduction	
2a	Enclose	T
2b	Engineered controls	
3	Organizational controls	O
4	PPE	P

Hazard assessment

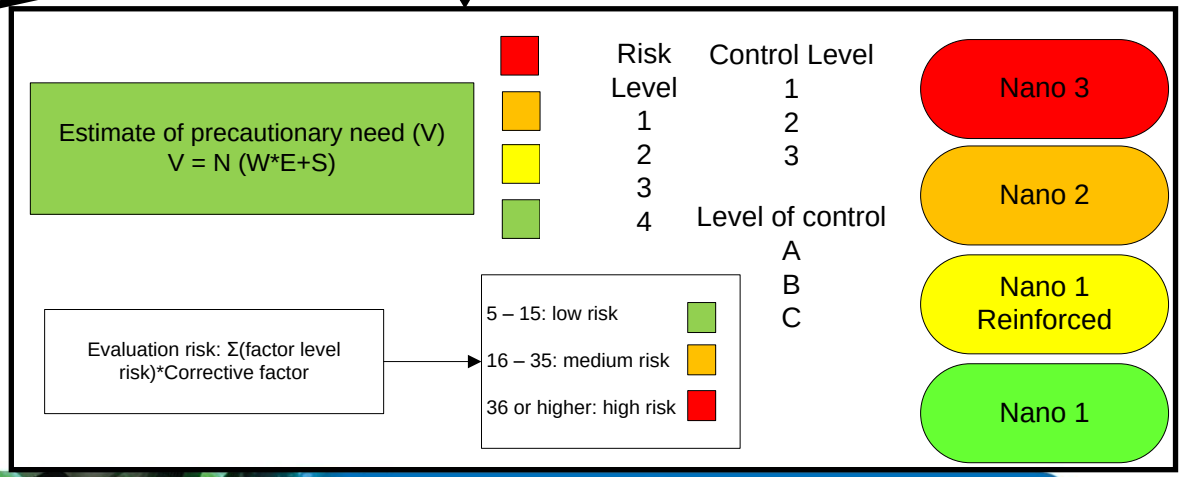
Used criteria:
Physical properties (size, shape, solubility)
Chemical properties (flammability, explosiveness)
Health related properties (Toxicity, Carcinogenicity)

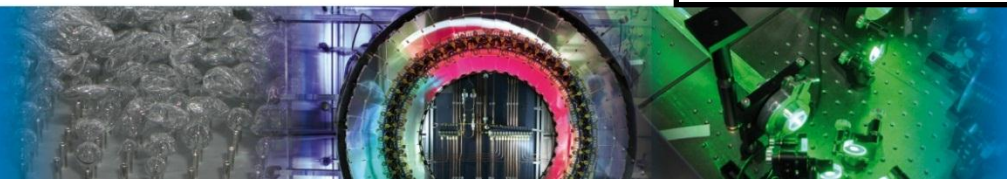
Exposure asssement

Used criteria:
Amount of used material,
Duration of the task,
Frequency, Dustiness etc

Risk evaluation (characterization)

Risk reducing measures





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Aim of the study

- Identify and list the available risk assessment methods for assessing the risks of ENP use;

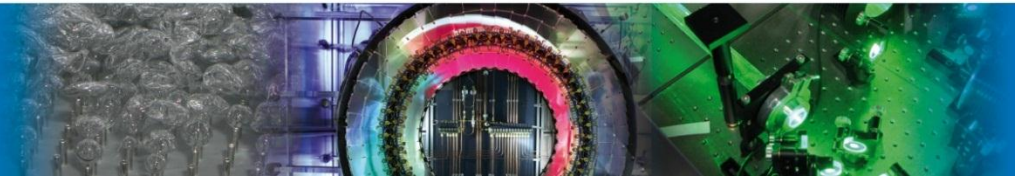
Literature study

- Evaluate and compare the most frequently used risk assessment methods theoretically and in the field;

Literature study
Comparison of criteria
Questionnaire

Studying four processes
Applying 10 risk ass. methods

- Determine which methods are appropriate for use in research institutes.



Literature study – Available Risk Assessment Systems

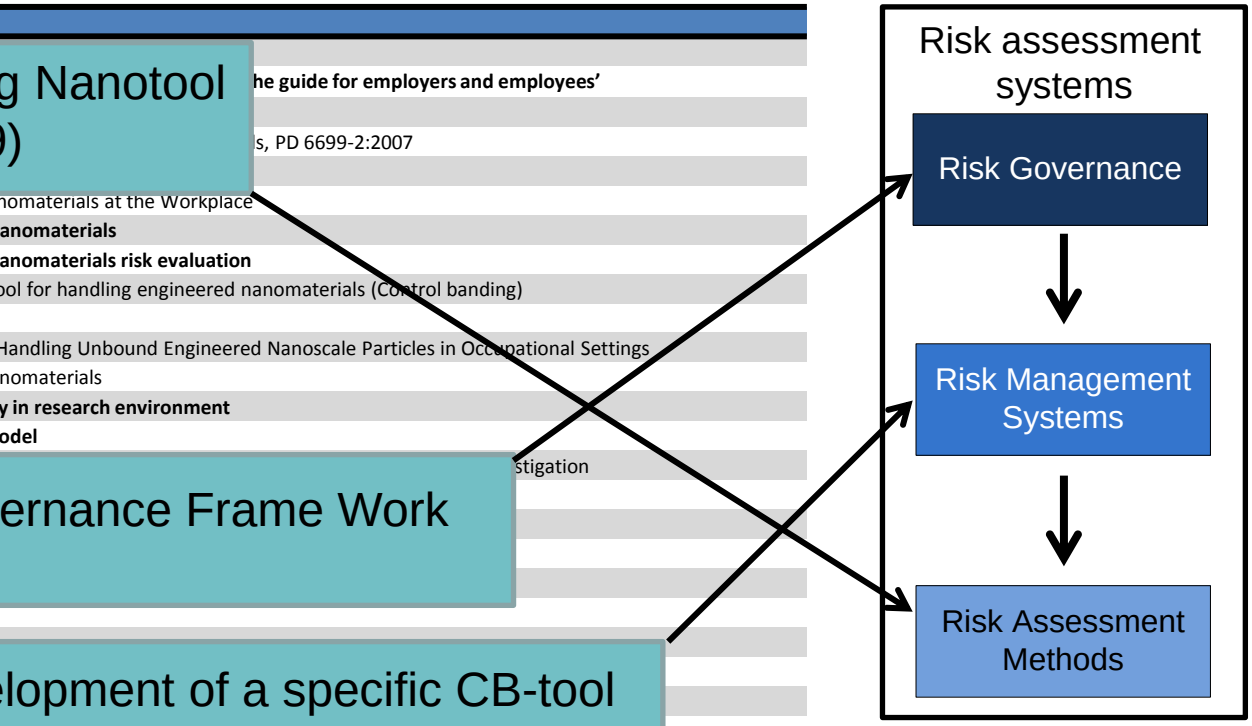
32 Risk assessment methods available for assessing risk of ENP-use (May 2012)

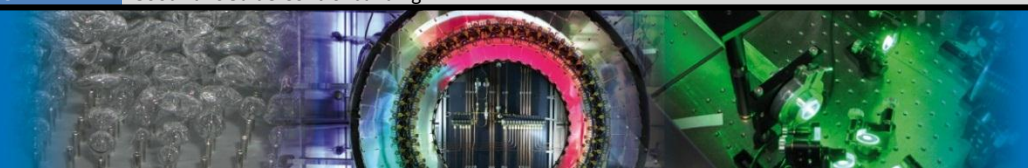
#	Name
1	
2	**he guide for employers and employees'**
3	
4	s, PD 6699-2:2007
5	
6	Guidance for Handling and Use of Nanomaterials at the Workplace
7	**Precautionary Matrix for Synthetic Nanomaterials**
8	**ISO/TR 13121, Nanotechnologies – Nanomaterials risk evaluation**
9	Work health and safety assessment tool for handling engineered nanomaterials (Control banding)
10	Risk identification framework
11	ASTM E2535 - 07 Standard Guide for Handling Unbound Engineered Nanoscale Particles in Occupational Settings
12	Risk-based classification system of nanomaterials
13	**Management of nanomaterials safety in research environment**
14	**Nanotechnology: Risk Assessment model**
15	stigation
16	
17	
18	
19	
20	**General Risk management system**
21&22	
23	
24	
25	
26	
27	
28	Tiered approach to an exposure measurement and assessment of nanoscale aerosols released form engineered nanomaterials in workplace operations [139]
29	**Nanotoolkit - Working Safely with engineered Nanomaterials in Academic Research Settings -**
30	Assured Nano
31	Safe handling and use of carbon nanotubes
32	GoodNanoGuide Control banding

Control Banding Nanotool (Zalk et al 2009)

IRGC Risk Governance Frame Work (IRCG 2007)

ANSES – Development of a specific CB-tool for nanomaterials (Riediker et al 2012)

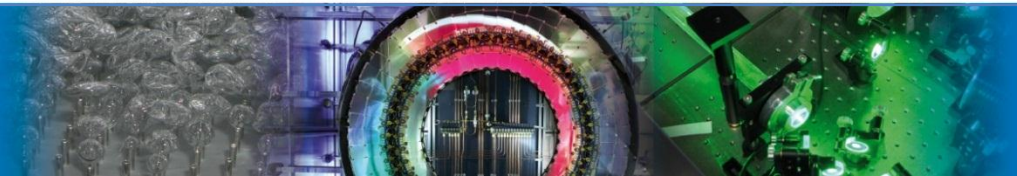




Selection of Risk Assessment Methods (RAMs)

11 of the 32 systems were selected for further study
Main criteria:
-Complete Risk Assessment Method
- 'Freely' available
-Developed for the assessing the risk of ENP-use
-Applicable to occupational settings
-Used in the field

Risk Assessment Method	Referred to as
ANSES, development of a specific control banding tool for nanomaterials	ANSES
Control Banding Nanotool	CB-Nanotool
General Risk Management System	Chemical Control Kit (CCK)
Guidance working safely with nanomaterials and nanoproducts 'the guide for employers and employees'	The Guidance
ISO/TR 13121, Nanotechnologies – Nanomaterials Risk Evaluation	ISO-TR13121
Management of Nanomaterials Safety in Research Environment	EPFL-model
Nanosafety Guidelines	TU-Delft guidel.
Nanotechnology: Risk Assessment Model	ISPESL-model
Nanotoolkit - – Working Safely with Engineered Nanomaterials in Academic Research Settings	Nanotoolkit
Precautionary Matrix for Synthetic Nanomaterials	PM
Stoffenmanager Nano	SM- nano



General comparison of the included RAMs

1. Comparison based on method

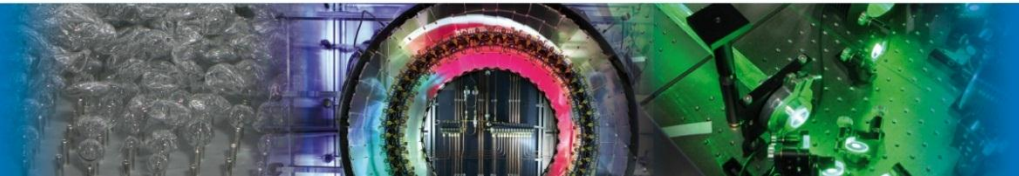
2. Comparison based on compagnies the RAMs were developed

Based on method

Three categories:

1. Based on the e-COSHH(Control Banding)-method;
2. Hazard assesement mainly based on physical properties;
3. Combination of 1 and 2.

	Toxicity level labelling				
	HB1	HB2	HB3	HB4	HB5
Classification & labelling	 **Warning** Eye irrit. 2 Skin irrit. 2 And all H-phrases not otherwise listed	 **Warning** Acute tox. 4  **Warning** STOT-SE 2	 **Warning** Acute tox. 3  **Warning** STOR-RE-2  **Danger** Skin corr. 1 Eye dam. 1  **Warning** Skin sens. 1 STOT-SE 3 (resp. irritant)	 **Warning** Acute tox. 1-2  **Danger** STOT-SE 1 STOT-RE 1 Repro tox 1A – 1B  **Warning** Carc. 2 Repro. 2	 **Danger** Resp sens. 1 Carc. 1A -1B Muta 1A – 1B  **Warning** Muta. 2



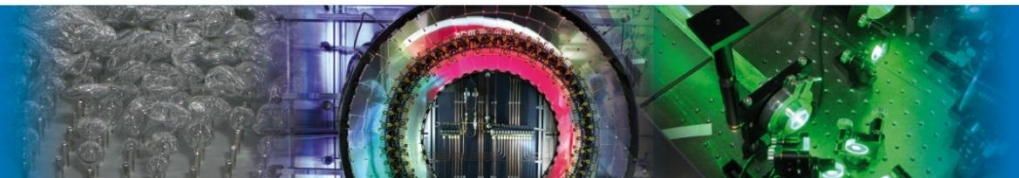
Comparison based on method

	Main factors for hazard assessment	*Based on:*
	Category 1	
CCK	Hazard code (R-phrases) , health-related properties	e-COSSH
CB-nanotool	Health-related properties, Shape	
SM- Nano	Hazard code (H- & R-phrases), health-related properties, shape	
ANSES	Hazard code (H- & R-phrases), health-related properties, shape	
	Category 2	
EPFL-model	Shape, used form (activity powder, suspension, matrix), aggregation	Mainly physical properties
PM	Redox/catalytic activity, stability	
TU-Delft Guidelines	Nano toxicity (general), pyrophoric effects	
The Guidance	Shape, solubility, persistence	
Nanotoolkit	Material state (solid, liquid and gas)	
	Category 3	
ISPESL-model	Toxicological properties (health-related effects), Fire & explosion, agglomeration/aggregation	Comb. of cat 1 & 2
ISO-TR13121	Toxicological properties (long and short term effects), Fire, explosion, flammability, corrosiveness, reactivity	

General comparison of the included RAMs

Companies for which the RAMs were developed

Companies	Risk Assessment Method
Small and Medium enterprises	The Guidance Chemical Control Kit ANSES Stoffenmanager nano PM
Industry	ISO-TR13121 Stoffenmanager nano PM The Guidance
Research/academic setting	EPFL-model Nanotoolkit CB-nanotool ISPESL-model TU-Delft guidelines



Risk assessment of occupational used nanomaterials

Criteria analysis for risk assessment

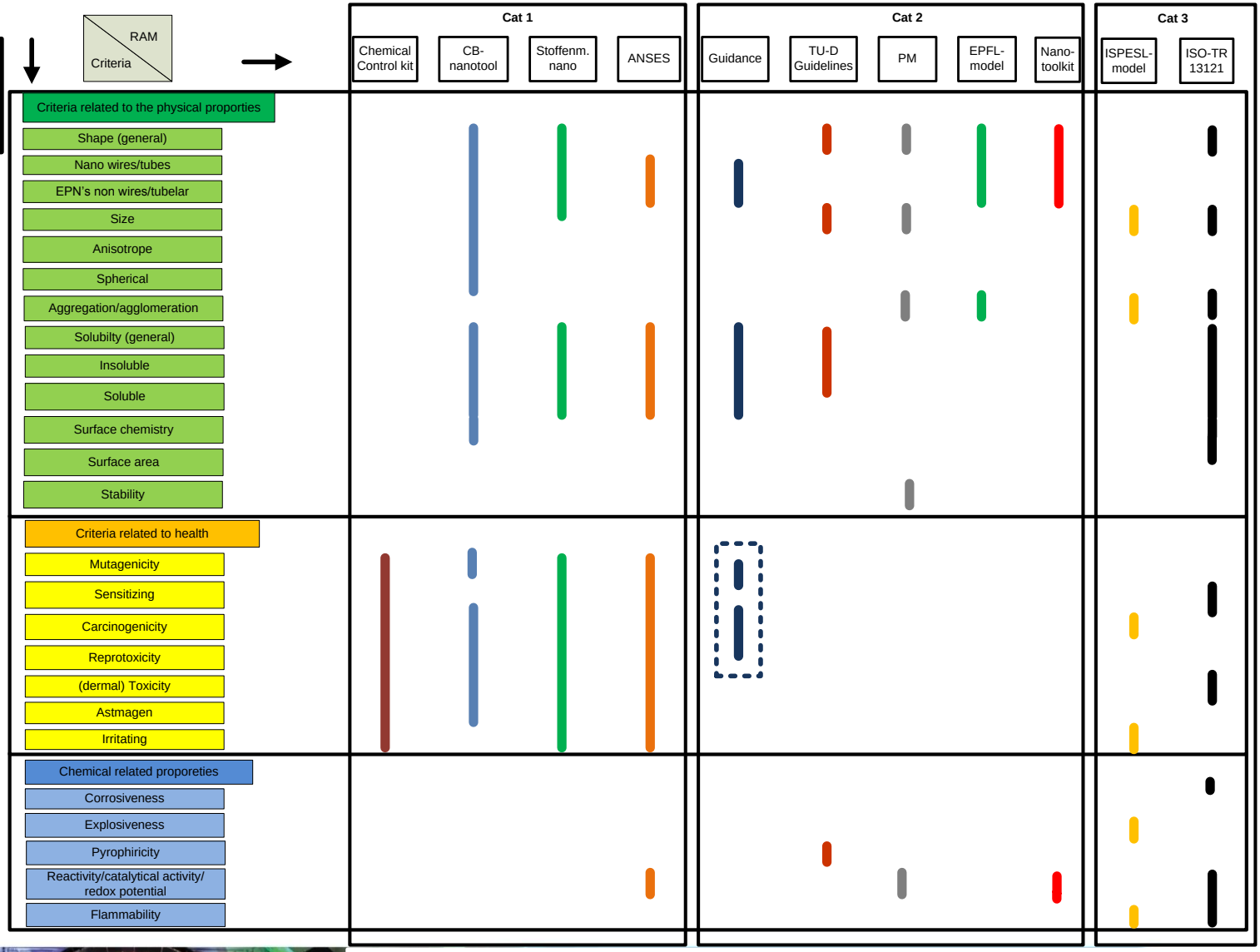
Results

Criteria for Hazard assessment

Physical related prop.
-Shape
-Size
-Aggregation/ agglomeration
-Solubility
-Surface area
-Surface chemistry

Health related prop.
- Mutagenicity
- Toxicity
- Carcinogenicity
- Irritating
- Reprotoxicity

Chemical related prop.
- Flammability
- Reactivity
- Corrosiveness
- Explosiveness



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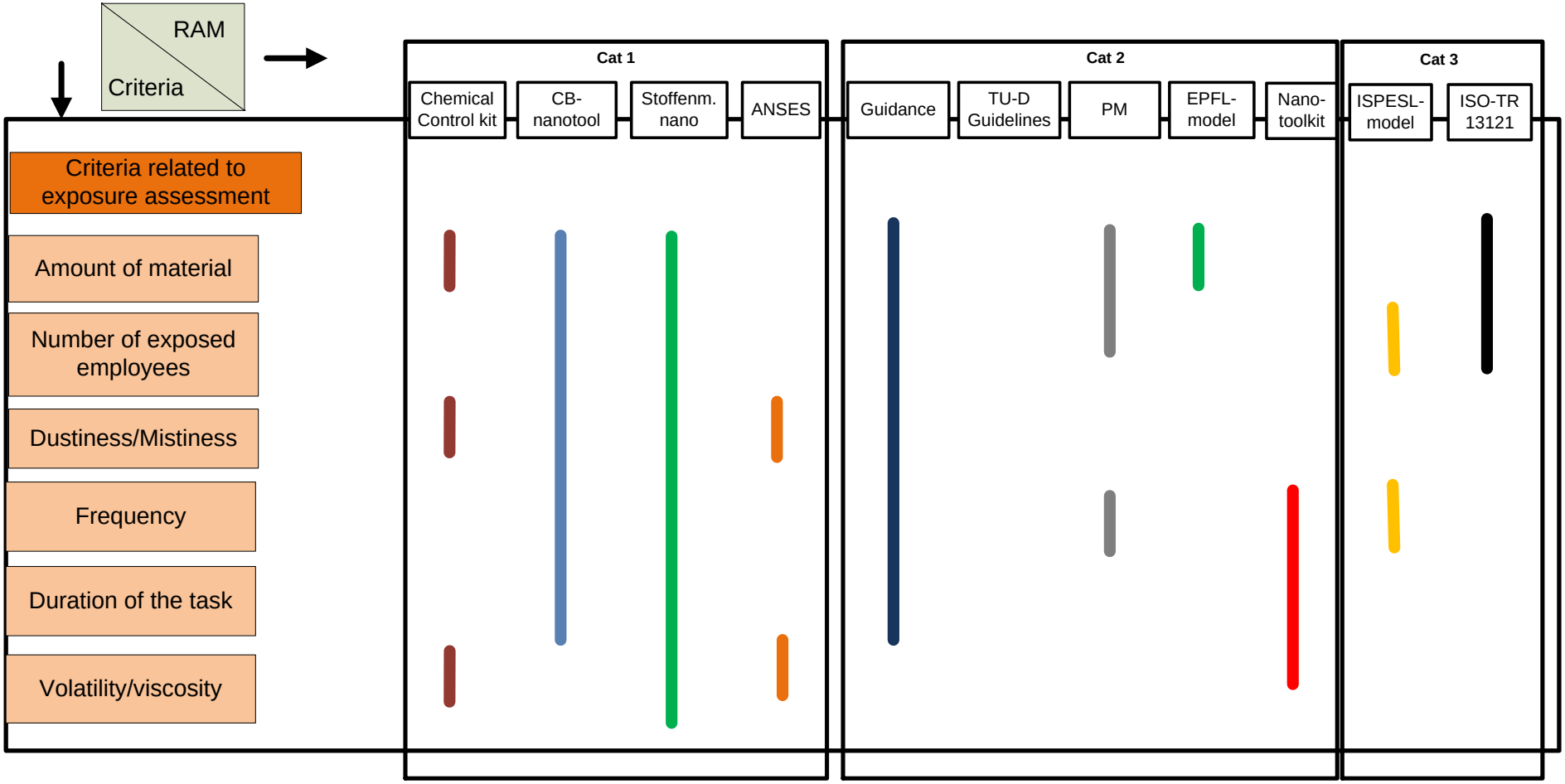
Results

Criteria for exposure assessment

Criteria analysis for risk assessment



Discussion: are one or two criteria adequate for exposure assessment?

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Field study – The use of RAMs at workplaces

Problem: how can the different RAMs be compared?

Comparing apples with pears????

Solution: Use the recommended risk reducing measures!

Field study – The use of RAMs at the workplace

Risk assessment	Chemical Control Kit	CB-Nanotool	SM-nano	ANSES	The Guidance	PM	Nano-toolkit	EPFL-model	ISPESL-model
Risk level	4	RL4	I	CL5	C	B	Cat 3	Nano3	High
	3	RL 3	II	CL4			Cat 2	Nano2	
	2	RL2		CL2 CL3	B			Nano 1ri	Middle
	1	RL1	III	CL1	A	A	Cat 1	Nano1	Low

TU-Delft guidelines: risk levels are not applied
ISO-TR13121 excluded: risk evaluation method not exactly defined

Studied processes:
Process 1: Use of nanoform SiO_2 at the UU
Process 2: Use of nanoform Al_2O_3-Co_3O_4 at the UvA
Process 3: Production and use of Si/SiO_2 at the TU-Delft
Process 4: Use of nanoform Cr_2O_3 and Co_3O_4 at the UG

Analysis of the process and the risk analysis
UU – use of nanoform SiO_2 in powder form and dispersion

Fume hood
Step 1: Sample of dry SiO_2 material

A sample of dry material (20 -30 mg) is transferred in a reaction tube.

Oven Closed Sytem
Step 2: Heating the sample up to 700°C

Heating the sample at 700°C for 5h.

Fume hood
Step 3: Dispersion of the sample in water/ethanol/NH_3/TPM
24h
Step 4: Cleaning the sample with ethanol

Dispersion of the sample in aqueous solution and after 24 h of incubation washing the sample with ethanol (3X) and dispersion of the sample in an aqueous solution.

Lab
Step 5: Sonication of the sample
30 – 60 min
Step 6: Determination of the concentration

Sonication of the sample for 30 – 60 minutes.

Determination of the concentration by pipetting 25-50 µl, drying and weighing the sample.

Fume hood
Step 7: Dispersion of sample in water/ ethanol/NH_3/TPM
o/n
Step 8: Cleaning the sample with ethanol

Dispersion of the sample in aqueous solution and after 24 h of incubation washing the sample with ethanol (3X) and dispersion of the sample in an aqueous solution.

Lab
Step 9: Pipetting sample on GRID
Step 10: Discarding the sample on the grid

Pipetting 25 µl of the sample on a grid for analysis (assumption: sample becomes dry).

Discarding the sample.

Frequency of handlings: once a day, Exposed persons: one
Risk reducing measures: All steps are performed in a lab with general ventilation.
Step 1, 3&4 and 7&8: performed in a fume hood.
Step 2: closed system (oven) .
Used PPE's: Safety goggles and gloves (each step)

TPM = 3-(Trimethoxysily)PropylMethacrylaat

	Step 1: Sample of dry SiO_2 material	**Step 2:** Heating the sample up to 700°C	**Step 3:** Dispersion of the sample in water/ethanol/NH_3/TPM → **Step 4:** Cleaning the sample with ethanol
	Step 1	Step 2	Step 3&4
1(CCK)			
2 (CB-nanotool)			
3 (SM-nano)	1 2	1 2	1 2
4 (ANSES)			
5 (Guidance)			
6 (PM)		X	
7 (EPFL)			
8 (ISPESL)			
9 (Nanotoolkit)			

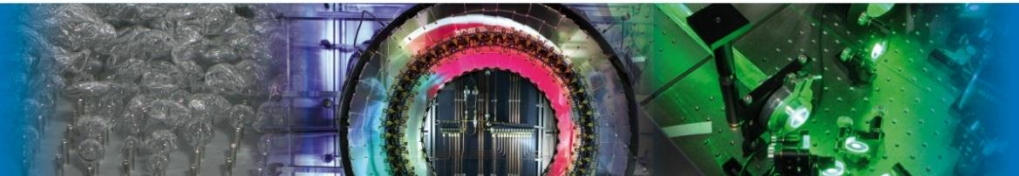
Results – Field study

Analysis of the process and the risk analysis
UU – use of nanoform SiO_2 in powder form and dispersion

Risk assessment	Chemical Control Kit	CB-Nanotool	SM-nano	ANSES	The Guidance	PM	EPFL-model	Nanotoolkit	ISPESL-model
Risk level Step 1	1	RL2	II (1) III (2)	CL4	B	B	Nano 3	Cat 2	Middle
Rec. RRM	none	none	NA	Containment	None	NA	none	none	NA
Risk level step 3&4	2	RL2	II (1) III (2)	CL2	B	B	Nano 1	Cat 1	Middle
Rec. RRM	none	none	NA	none	None	NA	none	none	NA
Risk level Step 5	2	RL2	II (1) III (2)	CL2 3 CL4 4	C	B	Nano 1	Cat 2	High
Rec. RRM	FH/LEV	FH/LEV	NA	CL2: LV CL4: containment	Prec. Principle	NA	FH	FH/BC	NA

Step 1: Handling 20 – 30 mg of dry SiO_2 in fume hood
Step 3&4: Dispersion of SiO_2 in a fume hood
Step 5: Sonication of SiO_2 in a open lab

BC: Biosafety Cabinet
FH: Fume Hood
LV: Local ventilation
LEV: Local Exhaust ventilation
NA: Not Applicable
Prec: Precautionary



Conclusions Part I

Available Risk Assessment Systems

- Over 32 systems are available for assessing risks of ENP-use;
- Risk Governance, Risk Management and Risk Assessment Methods.

In detailed studied Risk Assessment Methods

- 11 RAMs were studied in detailed;
- Only 4 of the studied RAMs were developed for use in a research environment.

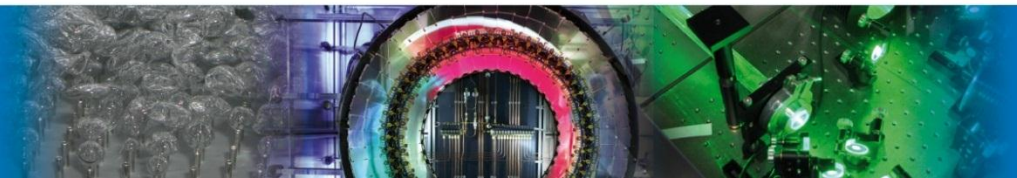
Used criteria for risk assessment in general

- A large variety of criteria are used for risk assessment.

(no standardization)

↓

ISO/DTS 12901-2
Nanotechnologies - Occupational risk management applied to engineered nanomaterials - Part 2: Use of the control banding approach



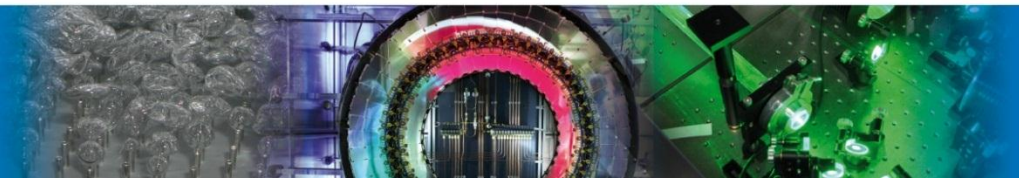
Conclusions Part II

Criteria for hazard assessment

- Some ENP specific criteria (e.g. surface area, agglomeration/aggregation) are often not used in RAMs;
- Chemical related criteria are most of the time not used.

Criteria for exposure assessment

- CB-nanotool, SM-nano and The guidance use almost all criteria for exposure assessment;
- Some RAMs (e.g. EPFL-model, ANSES, ISO-TR13121) use one or a few criteria for exposure assessment.



Conclusions Part III

Field study

- The risk level outcomes can deviate considerably for equal processes.
- A certain level of expertise is necessary for the use of the different RAMs

This is mainly caused by:

- The use of various criteria and/or differences in criteria interpretation lead to differences in risk level results;
- Differences in effect, of each criterion, on risk level determination, leading to different risk levels;
- Taking or not taking Risk Reducing Measures into account;
- Information used/ available during assessing the risks.

For example: Si

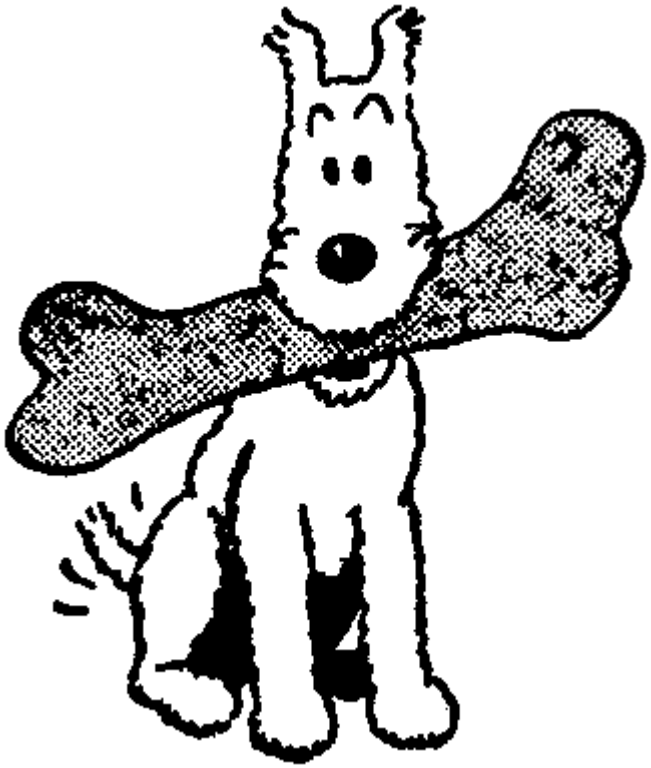
(ANSES) (CCK) 3 C → Hazard ← 1 A (ANSES) (CCK)

SDS	Io-li-tec nanomaterials [173]	Sigma-Aldrich [192] and Alfa Aesar [172]
Infor-mation	Flammable substance (H228), Skin corrosion/irritation (H315), Serious eye damage/eye irritation (H319) Specific target organ toxicity – single exposure: resp. tract irritation (H335).	Flammable substance (H228)

Recommendations

- Develop guidelines/manuals for the current RAMs
- Standardization of RAMs
- More research on ENP-specific properties
- Measurement of ENPs in research settings

Questions? …….



Many thanks for your attention