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RISK ASSESSMENT OF NANOCARBONS: USE OF ANALYTICAL HIERARCHY AND CONTROL BANDING APROACHES FOR SAFETY MANAGEMENT

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BROWN

University of São Paulo

Highlights

- Introduction
- Risks, reports and HSEnano website
- Multicriteria methods: control banding and AHP (Analytical Hierarchy Process)
- Nanocarbons & ranking using pairwise comparisons from judgment matrices
- Conclusions
- Acknowledgements

What is risk?

From Wikipedia ... 8 basic definitions ...

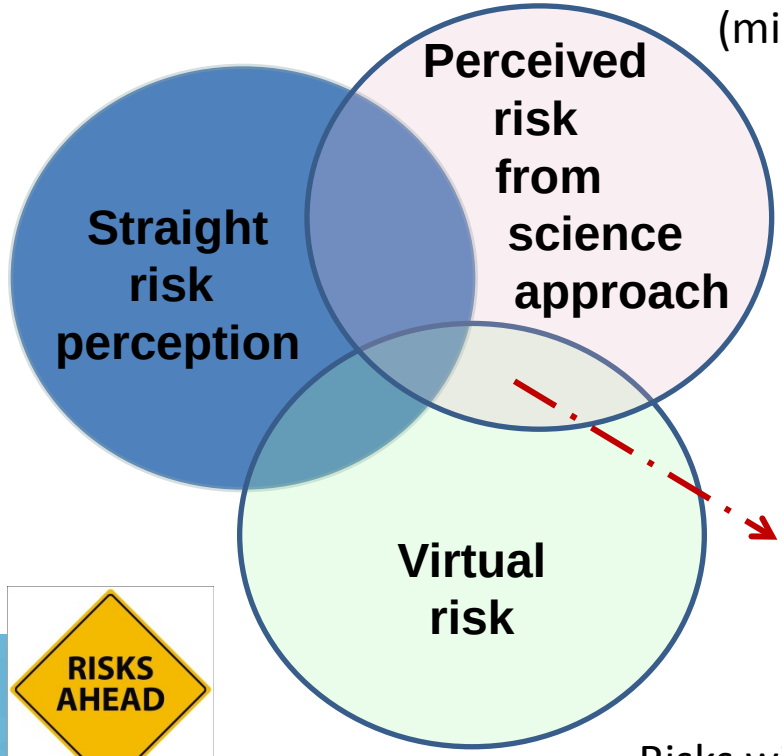
Oxford English Dictionary: (Exposure to) the **possibility of loss, injury, or other adverse or unwelcome circumstance**; a chance or situation involving such a possibility. (1655 AC)

Workplace: Product of the consequence and **probability of a hazardous** event or phenomenon. For example, the risk of developing cancer is estimated as the incremental probability of developing cancer over a lifetime as a result of exposure to potential carcinogens (cancer-causing substances).

It came from Italian word: "**riscare**" that means: navigate between hazardous rocks

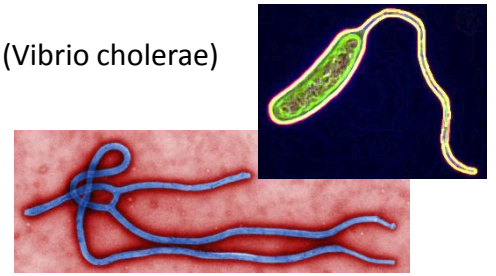
Risk perceptions

Type of risks



- Cholera contamination (microscope + trained person)

(Vibrio cholerae)



Source: http://www.cdc.gov/vhf/ebola

nanotechnology

Examples:
- Parachute diving
- Mountain climbing
- Driving

- Risks with insufficient certainties due its complexity or lack of acknowledgement
- Ex. Cellphone magnetic fields and health problems , global warming …

NIOSH 10 critical topics …

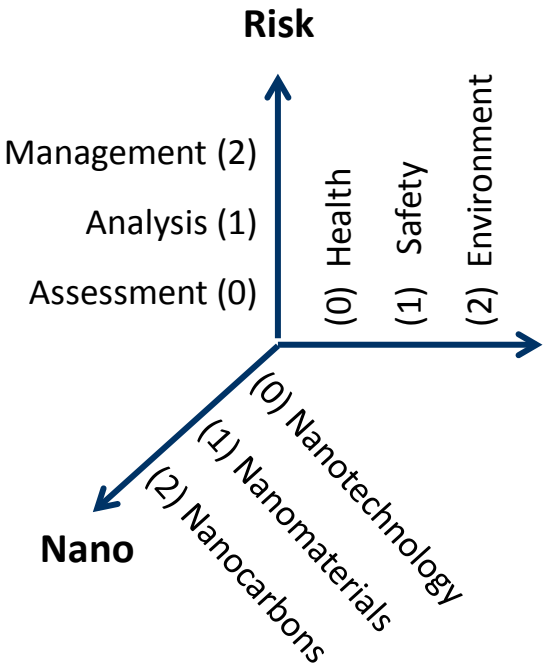
National Institute of Occupational Safety & Health

NIOSH has identified 10 critical topic areas to guide in addressing knowledge gaps, developing strategies, and providing recommendations.

Each topic provides a brief description of the research that NIOSH is conducting in the area of nanotechnology and the applications and implications of nanomaterials in the workplace.

- Toxicity and Internal Dose
- Risk Assessment
- Epidemiology & Surveillance
- Engineering Controls and PPE
- Measurement Methods
- Exposure Assessment
- Fire and Explosion Safety
- Recommendations & Guidance
- Global Collaborations
- Applications

Source: http://www.cdc.gov/niosh/topics/nanotech/critical.html



DOE (Design Of Experiments): Type: 3^k

Where:
- (0) : lower level
- (1) : central level
- (2) : higher level

Possible Permutations: (6)

R-N-H / H-N-R

R-H-N / N-H-R

H-R-N / N-R-H

	N	-	R	-	H		
	NANO		RISK		HSE	Google	YAHOO!
000	Nanotechnology		Risk assessment		Health	5.190.000	440.000
010	Nanotechnology		Risk analysis		Health	3.430.000	992.000
020	Nanotechnology		Risk management		Health	3.590.000	1.250.000
001	Nanotechnology		Risk assessment		Safety	1.630.000	244.000
011	Nanotechnology		Risk analysis		Safety	2.900.000	320.000
021	Nanotechnology		Risk management		Safety	2.550.000	472.000
002	Nanotechnology		Risk assessment		Environment	5.120.000	316.000
012	Nanotechnology		Risk analysis		Environment	4.150.000	805.000
022	Nanotechnology		Risk management		Environment	2.910.000	1.040.000
100	Nanomaterials		Risk assessment		Health	296.000	80.800
110	Nanomaterials		Risk analysis		Health	501.000	80.400
120	Nanomaterials		Risk management		Health	213.000	82.900
101	Nanomaterials		Risk assessment		Safety	261.000	61.600
111	Nanomaterials		Risk analysis		Safety	361.000	54.100
121	Nanomaterials		Risk management		Safety	190.000	60.500
102	Nanomaterials		Risk assessment		Environment	312.000	55.500
112	Nanomaterials		Risk analysis		Environment	447.000	63.200
122	Nanomaterials		Risk management		Environment	229.000	56.800
200	Nanocarbons		Risk assessment		Health	48.100	52.900
210	Nanocarbons		Risk analysis		Health	125.000	29.400
220	Nanocarbons		Risk management		Health	36.400	30.700
201	Nanocarbons		Risk assessment		Safety	94.200	1.620
211	Nanocarbons		Risk analysis		Safety	172.000	29.300
221	Nanocarbons		Risk management		Safety	35.500	29.200
202	Nanocarbons		Risk assessment		Environment	116.000	49.300
212	Nanocarbons		Risk analysis		Environment	198.000	65.200
222	Nanocarbons		Risk management		Environment	40.200	61.300

Words search (permutations using different databases and search engines)

Date: 11-May-2014

N	Word#1	Word#2	Word#3	Google	Yahoo	Web of Science	EBSCO	Capes	Library of Congress	European Commission	Brown University Library
	Palavra#1	Palavra#2	Palavra#3	Resultados (Google)	Resultados (Yahoo)	Resultados (Web of Science)	EBSCO (Biblioteca Pública de Providence/RI) (*)	Diretório de Periódicos Capes/Brasil	Biblioteca do Congresso dos EUA	Comissão Européia	Universidade Brown (Sistema - Biblioteca)
				http://www.google.com	http://www.yahoo.com	http://apps.isiknowledge.com	http://www.providlib.org/research-databases-0	http://www.periodicos.capes.gov.br/	http://catalog.loc.gov/	http://ec.europa.eu/geninfo/query/index.do?rulang=en	http://library.brown.edu/
				Google	Yahoo	Web of Science	EBESCO	Periódicos Capes	Library of Congress	European Comission	Brown University (Library)
	RISK	NANO	HSE	Google	Yahoo	Web of Science	EBSCO	Periódicos Capes	Library of Congress	European Comission	Brown Unibersity
a	Risk assessment			97.900.000	34.500.000	254.305	332.877	1.224.868	4.601	38.194	39.457
b	Risk analysis			398.000.000	60.700.000	623.680	517.982	2.544.310	2.386	28.621	70.798
c	Risk management			392.000.000	31.500.000	260.147	240.812	1.584.042	6.837	42.806	40.065
d		Nanotechnology		104.000.000	7.920.000	37.457	45.984	213.560	2.054	2.463	102.353
e		Nanomaterials		17.600.000	2.050.000	42.718	11.989	65.740	356	1.148	43.586
f		Nanocarbons		205.000	124.000	350	90	826	2	19	120.018
g			Health	1.050.000.000	478.000.000	1.641.371	3.881.796	8.471.335	>10.000	34.477	2.763.388
h			Safety	765.000.000	6.360.000.000	1.165.117	692.057	2.397.770	> 10.000	53.137	1.043.730
i			Environment	340.000.000	205.000.000	2.156.425	1.022.598	4.237.318	>10.000	101.287	2.454.346
1	Risk assessment	Nanotechnology	Health	2.240.000	455.000	215	338	3.692	0	511	4.495
2	Risk assessment	Nanotechnology	Safety	1.620.000	254.000	154	213	2.661	12	440	3.471
3	Risk assessment	Nanotechnology	Environment	5.540.000	313.000	135	202	3.229	7	388	4.647
4	Risk assessment	Nanomaterials	Health	298.000	65.900	279	316	2.098	8	484	2.798
5	Risk assessment	Nanomaterials	Safety	262.000	64.000	172	187	1.621	8	414	2.037
6	Risk assessment	Nanomaterials	Environment	313.000	65.800	216	237	1.897	4	362	2.780
7	Risk assessment	Nanocarbons	Health	46.400	31.200	0	0	41	0	2	27
8	Risk assessment	Nanocarbons	Safety	31.900	1.590	0	0	24	0	1	22
9	Risk assessment	Nanocarbons	Environment	110.000	31.200	0	0	38	0	2	25
10	Risk Analysis	Nanotechnology	Health	12.700.000	804.000	34	154	5.047	4	284	6.475
11	Risk Analysis	Nanotechnology	Safety	3.450.000	310.000	50	96	3.342	6	193	4.661
12	Risk Analysis	Nanotechnology	Environment	4.020.000	596.000	59	119	4.803	3	230	7.055
13	Risk Analysis	Nanomaterials	Health	409.000	82.600	118	154	2.419	1	177	3.661
14	Risk Analysis	Nanomaterials	Safety	361.000	55.900	60	82	1.760	2	151	2.518
15	Risk Analysis	Nanomaterials	Environment	445.000	62.800	90	148	2.441	1	152	3.886
16	Risk Analysis	Nanocarbons	Health	112.000	33.400	0	0	54	0	2	35
17	Risk Analysis	Nanocarbons	Safety	170.000	1.810	0	0	35	0	1	28
18	Risk Analysis	Nanocarbons	Environment	195.000	76.900	0	0	56	0	2	37
19	Risk Management	Nanotechnology	Health	2.370.000	1.250.000	92	160	3.326	5	389	3.300
20	Risk Management	Nanotechnology	Safety	2.250.000	430.000	59	119	2.363	5	306	2.584
21	Risk Management	Nanotechnology	Environment	5.710.000	963.000	46	127	3.018	3	354	3.515
22	Risk Management	Nanomaterials	Health	217.000	83.100	84	100	1.912	1	288	1.430
23	Risk Management	Nanomaterials	Safety	192.000	66.000	50	89	1.013	2	250	1.168
24	Risk Management	Nanomaterials	Environment	233.000	57.700	42	100	1.106	1	248	1.460
25	Risk Management	Nanocarbons	Health	35.200	31.100	0	0	20	0	2	9
26	Risk Management	Nanocarbons	Safety	34.300	1.630	0	0	13	0	2	10
27	Risk Management	Nanocarbons	Environment	38.700	1.720	0	0	21	0	2	9

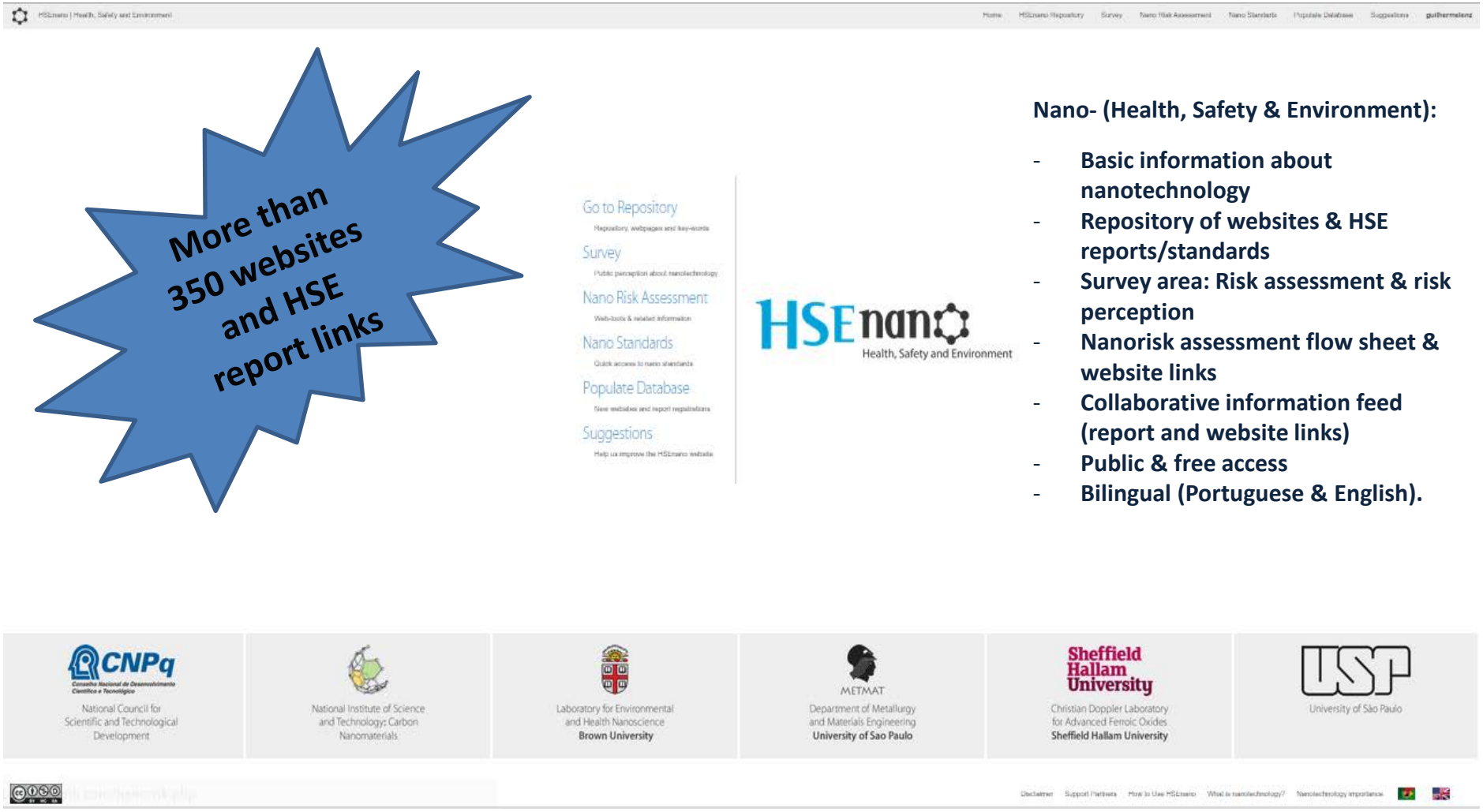
Bibliographic review: focussing on reports ~ last 10 years

- Using DOE planning (Design of Experiments choosing key words and its combinations and permutations) and internet searching tools :
- University databases : journals impact factor; citations, etc.
- Words: risk, assessment, toxicology, nanotechnology, nanocarbons (graphene, CNT, SWNT, MWNT, DWNT, graphene, fullerene, carbon black, few layers graphene, etc.) …;
- Agencies and countries: ILO-UN, US-OSHA, US-EPA, UN, EU, HSE/UK, Australia, Japan, Swiss, Netherlands, etc.

http://www.hsenano.org;

www.hsenano.com

www.hsenano.info (registered website domain under construction and evaluation)



Nano- (Health, Safety & Environment):

- **Basic information about nanotechnology**
- **Repository of websites & HSE reports/standards**
- **Survey area: Risk assessment & risk perception**
- **Nanorisk assessment flow sheet & website links**
- **Collaborative information feed (report and website links)**
- **Public & free access**
- **Bilingual (Portuguese & English).**

How big is the nanomaterial risk issue problem?

Chemical Abstracts Service

Date: 05/23/2014 – 19:33pm

Nanotech

Nano-functionalization

Combinations of chemicals in new products

(...)

workers suffer more than 190,000 illnesses and 50,000 deaths annually related to chemical exposures.

Source: https://www.osha.gov/dsg/safer_chemicals/index.html

OSHA Transitioning to safer chemicals

(OSHA: Occupational Safety & Health Administration)

nanoSAFE'14 BROWN USP University of São Paulo

New materials , "new" risks … we need new approaches to deal with them !

http://2020science.org/2011/08/09/what-was-worrying-us-about-nanotechnology-safety-seven-years-ago

What is Control Banding (CB) and how it works

IAHA (The American Industrial Hygiene Association): **Control banding is a complementary approach to protecting worker health** by utilizing finite resources to identify and implement exposure controls. Given the reality that appropriate occupational exposure limits cannot be established for every chemical in use, a **chemical is assigned to a "band" for control measures**, based on **its hazard classification** according to international criteria, the amount of chemical in use, and its volatility/dustiness

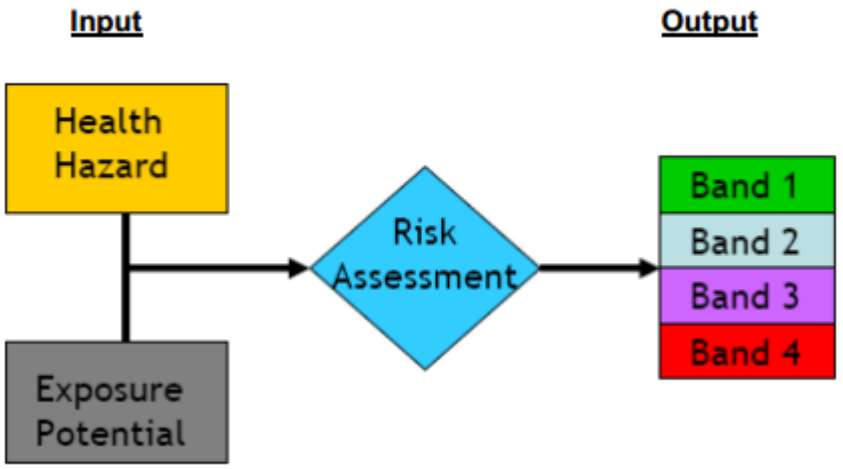
There is no single such thing or methodology defined as "control banding"

Frequently evaluation = air sampling
Take a measurement & compare it to the exposure limit.

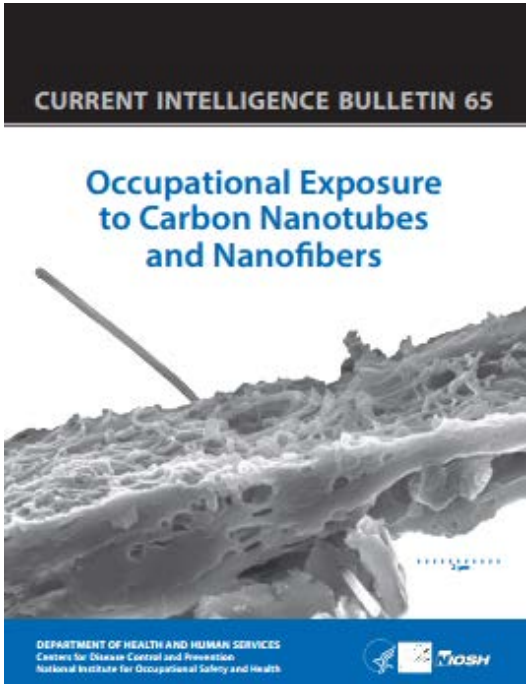
if > PEL than fix it !
if < PEL: "not a problem"
if no PEL: **???? …**

Thousands of chemicals, only 500 with PELs

(*) PEL: **Permissible Exposure Limits**

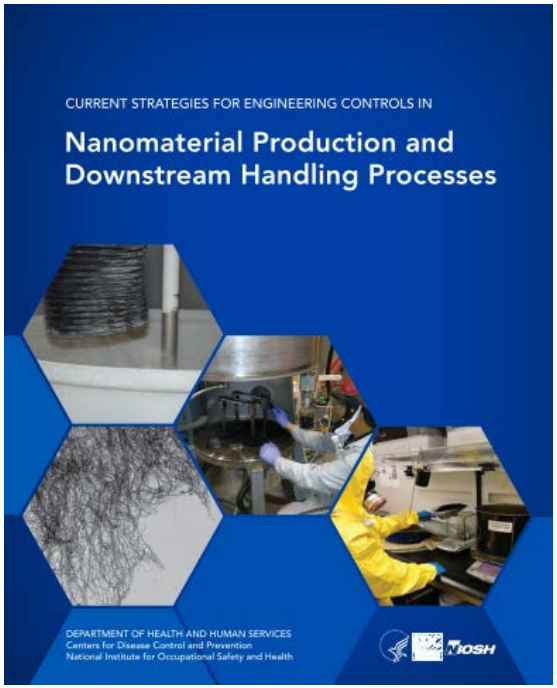


Source: https://www.osha.gov/dsg/annotated-pels/tablez-1.html



April 2013

According to NIOSH, due to some residual risk at the **REL (recommended exposure limit)** and the uncertainty related to chronic health effects, **exposures to CNT and CNF should be reduced "as much as possible"— below 1 µg/m³ of respirable elemental carbon as an 8 - hour TWA during a 40 - hour workweek.**



November 2013

Currently (2014), there are **no established regulatory occupational exposure limits (OELs) for nanomaterials in the United States**; however, other countries have established standards for some nanomaterials, and some companies have supplied OELs for their products

Source: CDC / NIOSH

Example Benchmark Particles & Risk-based Exposure Bands: Poorly-Soluble Inhaled Particles

Hazard Rank	Substance	Primary Particle Size	Occupational Exposure Band* (8-hr TWA, µg/m³)
Low	Molybdenum oxide Titanium dioxide (F)	Fine	>1,000
Moderate	Carbon black Diesel exhaust particulate Titanium dioxide (UF)	Ultrafine	100 – 1,000
High	Nickel oxide	Fine	10 – 100
Very high	Nickel subsulfide Gallium arsenide	Fine	1–10

*Assignment based on working lifetime exposures associated with <1/1000 excess risk of lung cancer; 95% LCL estimates extrapolated from rat chronic inhalation studies by NTP [Kuempel et al 2012, JNR 14:1029].

Just remember !
For CNT (US-NIOSH):

REL: 1µg/m³

Source:

Strategies for Occupational Exposure Limits for Engineered Nanomaterials

Eileen D Kuempel PhD, Vincent Castranova PhD, Charles L Geraci PhD, Paul A Schulte PhD
National Institute for Occupational Safety and Health

Lancet Oncol 2014

Published Online
October 31, 2014
http://dx.doi.org/10.1016/S1470-2045(14)71109-X

As a whole, the Working Group acknowledged that the above mechanisms are all relevant to humans. However, a majority did not consider the mechanistic evidence for carcinogenicity—especially concerning chronic endpoints—to be strong for any specific CNT. Furthermore, the lack of coherent evidence across the various distinct CNTs precluded generalisation to other types of CNTs. Thus, MWCNT-7 was classified as possibly carcinogenic to humans (Group 2B); and SWCNTs and MWCNTs excluding MWCNT-7 were categorised as not classifiable as to their carcinogenicity to humans (Group 3).

Remark: MWCNT-7 ; Multiwall carbon nanotube from Mitsui/Japan.

The **British Standard Institute** has suggested benchmark exposure levels for four nanoparticle hazard types:

- For insoluble nanomaterials a general benchmark level of **0.066 × OEL** of the corresponding microsized bulk material (expressed as mass concentration) is proposed;

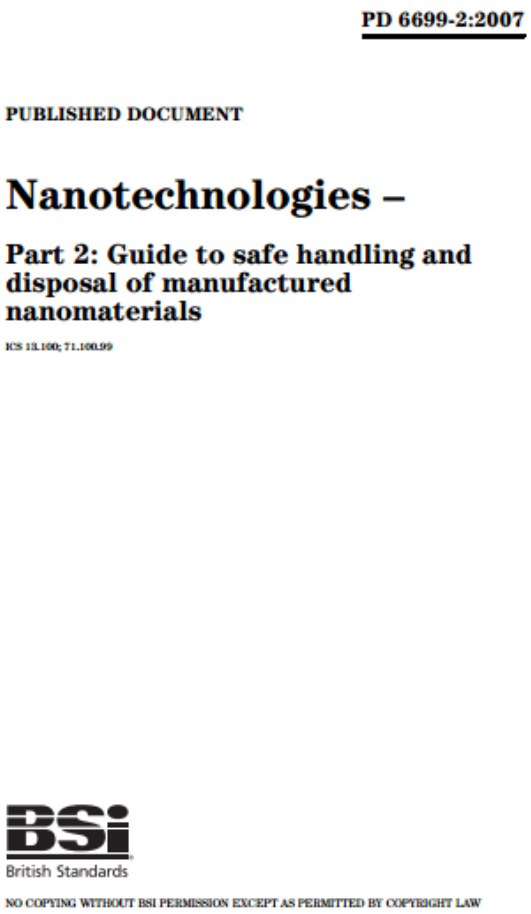
- For fibrous nanomaterials the proposed benchmark level is **0.01 fibres/ml**;

- For highly soluble nanomaterials a benchmark of **0.5 × OEL** is proposed;

- For substances classified as carcinogenetic, mutagenic, asthmagenic or reproductive (CMAR) in their coarse form, the same hazards will be considered for the nano form and the suggested benchmark level is **0.1 × OEL** (mass concentration) of the corresponding microsized material.

OEL: Occupational Exposure Level

Multiplicative risk factors



PD 6699-2:2007

PUBLISHED DOCUMENT

Nanotechnologies –

Part 2: Guide to safe handling and disposal of manufactured nanomaterials

ICS 13.100; 71.100.99

BSI British Standards

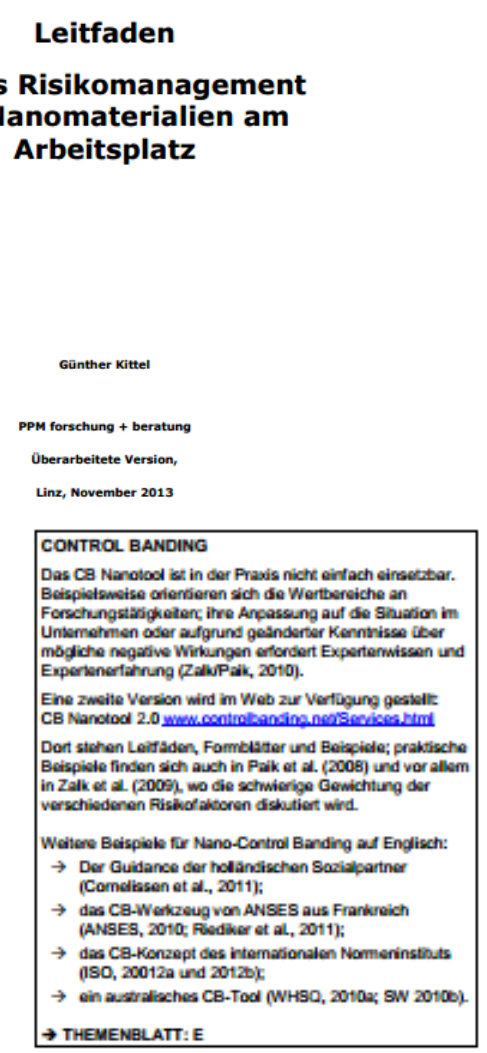
Source: BSI/UK

The German Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) has also developed recommendations for benchmark limits, using size and density of the nanoparticles as classification criteria. IFA proposed the following benchmark limits as increases over the background exposure to ultrafine particles during a 8-hour working shift, based upon its experience in measurement and the detection limits of the measurement methods currently employed:

- For metals, metal oxides and other biopersistent granular nanomaterials with a density of > 6,000 kg/m^3, a particle number concentration of **20,000 particles/cm^3 in the range of measurement between 1 and 100 nm should not be exceeded.**

- For biopersistent granular nanomaterials with a density below 6,000 kg/m^3, a particle number concentration of 40,000 particles/cm^3 in the measured range between 1 and 100 nm should not be exceeded.

- For carbon nanotubes (CNTs) for which no manufacturer's declaration is available that the CNTs have been tested as safe against asbestos-like effects**, a provisional fiber concentration of 10,000 fibres/m^3 is proposed for assessment**, based upon the exposure risk ratio for asbestos.



Leitfaden

für das Risikomanagement von Nanomaterialien am Arbeitsplatz

Günther Kittel

PPM forschung + beratung

Überarbeitete Version,

Linz, November 2013

CONTROL BANDING

Das CB Nanotool ist in der Praxis nicht einfach einsetzbar. Beispielsweise orientieren sich die Wertbereiche an Forschungstätigkeiten; ihre Anpassung auf die Situation im Unternehmen oder aufgrund geänderter Kenntnisse über mögliche negative Wirkungen erfordert Expertenwissen und Expertenerfahrung (Zalk/Paik, 2010).

Eine zweite Version wird im Web zur Verfügung gestellt: CB Nanotool 2.0 www.controlbanding.net/Services.html

Dort stehen Leitfäden, Formblätter und Beispiele; praktische Beispiele finden sich auch in Paik et al. (2008) und vor allem in Zalk et al. (2009), wo die schwierige Gewichtung der verschiedenen Risikofaktoren diskutiert wird.

Weitere Beispiele für Nano-Control Banding auf Englisch:

- → Der Guidance der holländischen Sozialpartner (Cornelissen et al., 2011);
- → das CB-Werkzeug von ANSES aus Frankreich (ANSES, 2010; Riediker et al., 2011);
- → das CB-Konzept des internationalen Normeninstituts (ISO, 2012a und 2012b);
- → ein australisches CB-Tool (WHSQ, 2010a; SW 2010b).

→ **THEMENBLATT: E**

Control Banding Approaches for Nanomaterials

6 online/web tools

Table 1. Summary of the most important characteristics of the various CB tools

		Hazard banding				Exposure banding								Matrix
		Allocation system				Source domains/type of activities*					Number of bands/levels			
	CB tool Short name	Binary	Score	*N*	Synthesis	Powder handling	Application ready-to-use products	Abrasion	Emission potential	Exposure potential	*N*	CB	RL	
1	Precautionary Matrix	–	+	1	(+)	(+)	(+)	(+)	+	–	1	2	–	
2	NanoTool	–	+	4	+	+	–	–	+	–	4	4	–	
3	ANSES	+		5	(+)	+	+	+	+	–	4	5	–	
4	Stoffenmanager Nano	+	–	5	+	+	+	(+)	–	+	4	–	3	
5	NanoSafer	+	+	4	–	+	–	–	–	+	5		5	
6	Guidance	+	–	3	+	+	+	+	+	–	3	3	–	

*Based on Schneider *et al.* (2010).

1 Precautionary matrix does not distinguish separate hazard and exposure bands.

N Number of bands.

CB Control band.

RL Risk level.

+ Used/addressed by tool.

– Not used/addressed by tool.

(+) only implicitly addressed by tool.

Source:

Control Banding Approaches for Nanomaterials

DERK H. BROUWER[1]

Ann. Occup. Hyg., Vol. 56, No. 5, pp. 506–514, 2012

doi:10.1093/anhyg/mes039

FRANCE:

ANSES (French Agency for Food, Environmental and Occupational Health & Safety)

Bandes de danger	Bandes de potentiel d'émission			
	PE1	PE2	PE3	PE4
BD1	NM1	NM 1	NM 2	NM 3
BD2	NM1	NM 1	NM 2	NM 3
BD3	NM1	NM 1	NM 3	NM 4
BD4	NM 2	NM 2	NM 4	NM 5
BD5	NM 5	NM 5	NM 5	NM 5

- **NM 1 : Ventilation générale naturelle ou mécanique.**
- **NM 2 : Ventilation locale :** hotte d'extraction, hotte à fente d'aspiration horizontale, bras d'aspiration, table aspirante, *etc.*
- **NM 3 : Ventilation fermée :** cabine ventilée, hotte de laboratoire, réacteur fermé avec ouverture fréquente.
- **NM 4 : Confinement total :** systèmes fermés en continu.
- **NM 5 : Confinement total et examen par un spécialiste exigé :** demander le conseil d'un expert.

Source: ANSES/ France

USA:

CDC (Centers for Disease Control and Prevention)
NIOSH (National Institute for Occupational Safety and Health)

Lawrence Livermore National Laboratory

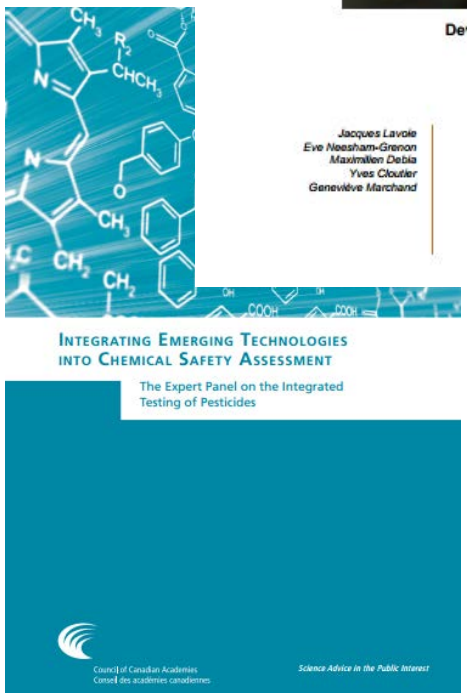
Control Banding Nanotool:
Evaluation of a qualitative risk assessment method for the control of nanoparticulate exposures

Exposure Duration	Bound Materials	Potential Release	Free / Unbound
Hazard Group A (Known to be inert)			
Shout	1	1	2
Medium	1	1	2
Long	1	2	2
Hazard Group B (Understand reactivity/function)			
Short	1	2	2
Medium	1	2	3
Long	1	3	3
Hazard Group C (Unknown Properties)			
Short	2	2	3
Medium	2	3	4
Long	2	4	4

Band 1: Use good industrial hygiene practice and general ventilation.
Band 2: Use an engineering control, typically local exhaust ventilation.
Band 3: Enclose the process.
Band 4: Seek expert advice.

Sources: CDC/NIOSH and LLN laboratory

Canada: The Institut de Recherche Robert-Sauvé en Santé et en Sécurité du Travail



Legislation: Pest Control Products Act (PCPA)

* Including nanomaterials

Score	Generation rate bands	
	Probability of inhalation	Examples
8.0	Very high	Uncontrolled aerosolization of the biological contaminant; proximity to emission sources; work in the emission plumes; medical procedures producing aerosols or other similar situations
6.0	High	High aerosolization; decontamination work; care given to an infectious patient coughing or sneezing with mouth uncovered or other similar situations
4.0	Moderate	Moderate aerosolization; contact with the biological contaminant; long distance from the source; infectious patient coughing or sneezing with mouth covered or other similar situations
2.0	Low	Low aerosolization; personnel assigned to other care tasks
0	None	No aerosolization

Sources: IRSST and Council of Canadian Academies /Canada

Australia: Safe Work Australia Agency

www.worksafe.qld.gov.au

Workplace Health and Safety Queensland

Nanomaterial control banding tool worksheet

Workplace details		De-identification number:
Description of nanomaterial (type, form, etc)		
Details of the parent material/s	*(Chemical name, CAS number, risk and safety phrases, from material safety data sheet, or similar)*	
Production description	*(e.g. vapour phase, solid phase, liquid phase techniques)*	
Task description		
Date		
Control banding team members		

Department of Justice and Attorney-General

Queensland Government

safe work australia

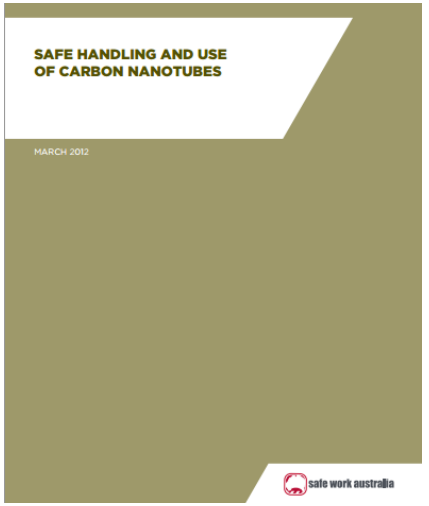


Table 3 – Matrix to Determine the Control Band (1-4)

Exposure Potential

Determining the exposure potential, and hence the recommended control band, based on the quantity of CNTs handled, and the likelihood that CNTs will become airborne.

	High Assessed Exposure	Moderately High Assessed Exposure	Moderately Low Assessed Exposure	Low Assessed Exposure
Quantity A	4	4	3	2
Quantity B	4	3	3	2
Quantity C	4	3	2	1
Quantity D	3	2	1	1

Source: Safe Work Australia

Switzerland: The Federal Office of Public Health (FOPH) - Federal Department of Home Affairs

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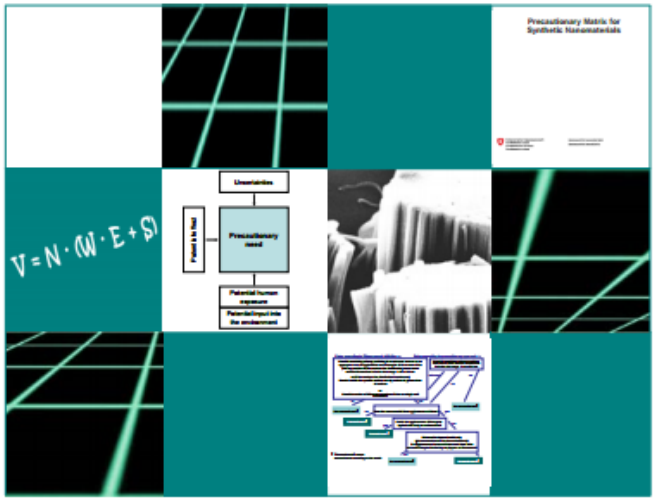
Guidelines on the Precautionary Matrix for Synthetic Nanomaterials



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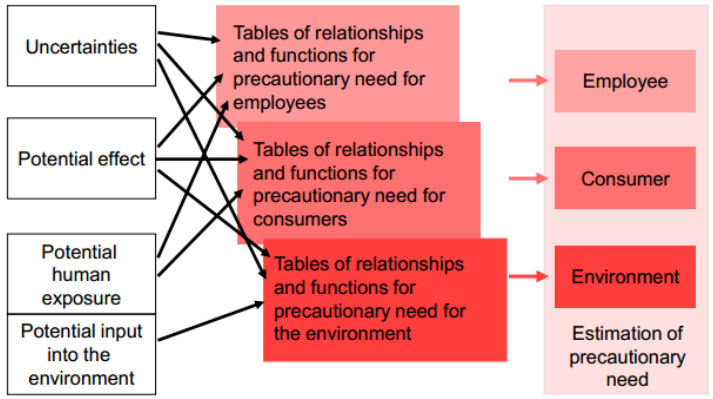

Guidelines

on the

Precautionary Matrix for Synthetic Nanomaterials

Version 1.1

Version 3.0
16 September 2013

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Federal Office of Public Health FOPH
Federal Office for the Environment FOEN

Reactivity				
	High	If exposure via the lungs probable: information on acute inhalation toxicity required	If exposure via the lungs probable: information on acute inhalation toxicity required If accumulative: data on long term effects required	If exposure via the lungs probable: information on acute inhalation toxicity required If accumulative: data on long term effects required
	Medium	If exposure via the lungs probable: information on acute inhalation toxicity required	If exposure via the lungs probable: information on acute inhalation toxicity required If accumulative: data on long term effects required	If exposure via the lungs probable: information on acute inhalation toxicity required If accumulative: data on long term effects required
	Low	No further nanospecific testing required	No further nanospecific testing required	No further nanospecific testing required
		Low	**Medium**	**High**
		Stability		

Source: FOPH / Swiss

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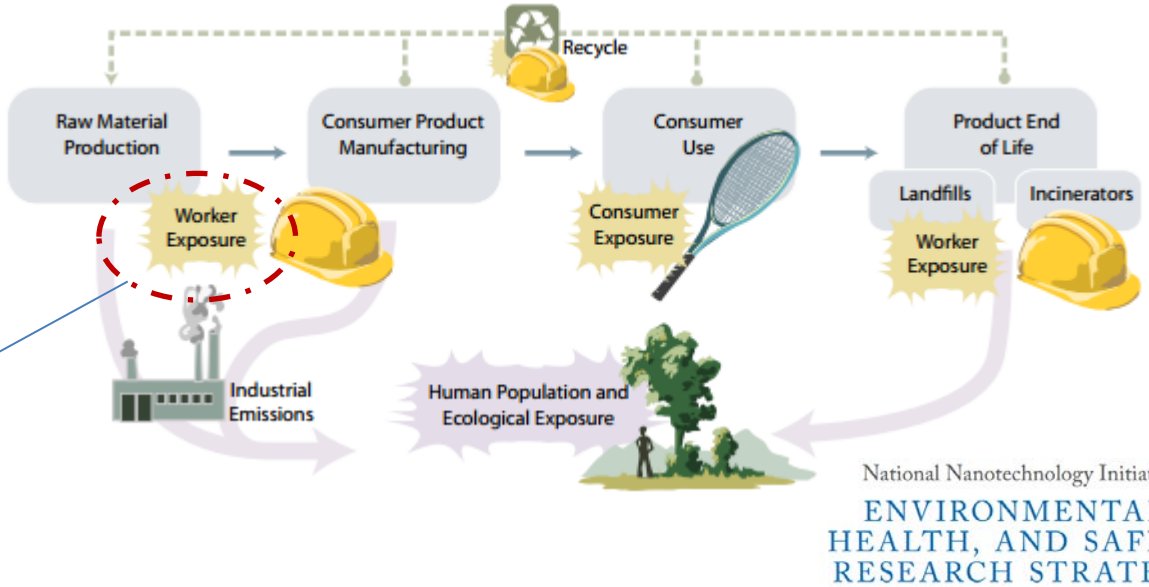
Emerging Contaminants – Nanomaterials
December 2010

Source: US EPA



Worker/ Environmental Hazard + Release/ Exposure Probability = Risk (Degree of Hazard) Level

AHP

Improve the quality of hazards modeling: Quantitative control level

Nanomaterials

Environmental Hazard	Release Probability: Unlikely (1)	Low (2)	Likely(3)	Probable (4)
Very High or Unknown (D)	Control Level III	Control Level III	Control Level IV	Control Level IV
High (C)	Control Level II	Control Level II	Control Level III	Control Level IV
Medium (B)	Control Level I	Control Level I	Control Level II	Control Level III
Low (A)	Control Level I	Control Level I	Control Level I	Control Level II

What is AHP and How it works?

The AHP (**A**nalytic **H**ierarchy **P**rocess) is a multicriteria method created by Thomas L. Saaty (University of Pittsburgh) in 1971. The AHP has the following approach:

- **Decomposing a decision into smaller parts:** one overall goal on the top level, several decision alternatives on the bottom level and several criteria contributing to the goal

- **Pairwise comparisons on each level; Comparing pairs** of alternatives with respect to each criterion *and* pairs of criteria with respect to the achievement of the overall goal.

- **Synthesizing judgments**.: Obtaining priority rankings of the alternatives with respect to each criterion and the overall priority ranking for the problem.

Pairwise comparisons:

	to A1	A2	A3
Alternative 1 (A1)	a_{11}	a_{12}	a_{13}
Alternative 2 (A2)	a_{21}	a_{22}	a_{32}
Alternative 3 (A3)	a_{31}	a_{32}	a_{33}

(a) $a_{ii} = 1$

A comparison of criterion i with itself:

equally important

(b) $a_{ij} = 1/ a_{ji}$

a_{ji} are reverse comparisons and must be the reciprocals of a_{ij}

→ Pairwise Comparison Matrix : $A = (a_{ij})$

Values for a_{ij} :

Numerical values	Verbal judgement of preferences
1	equally important
3	weakly more important
5	strongly more important
7	very strongly more important
9	absolutely more important

2,4,6,8 => intermediate values

reciprocals => reverse comparisons

1 to 9 - scale

The human brain can deal only with 7 +/- 2 things at the same time !

If you increase the number of pairs to compare .. You will lose accuracy.

Weber-Fechner law: $M = a*\log s + b$; $a \neq 0$
M – sensation and s – stimuli.

Structuring a hierarchy:

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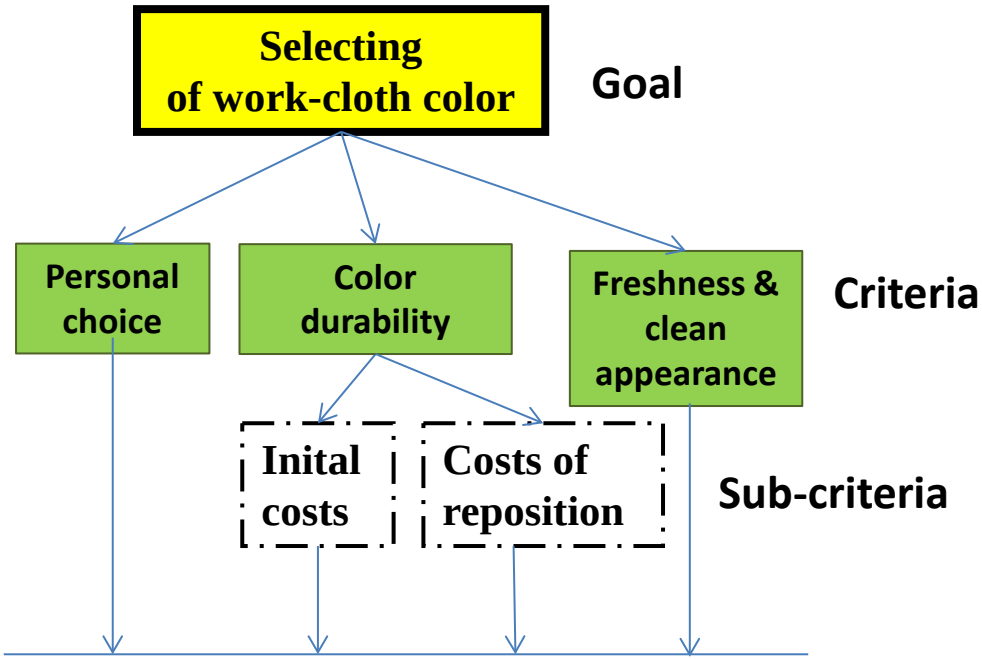
e.g. Let's create a scale (rank) of preferences between colors:

Numerical values	Verbal judgement of preferences
1	equally important
3	weakly more important
5	strongly more important
7	very strongly more important
9	absolutely more important



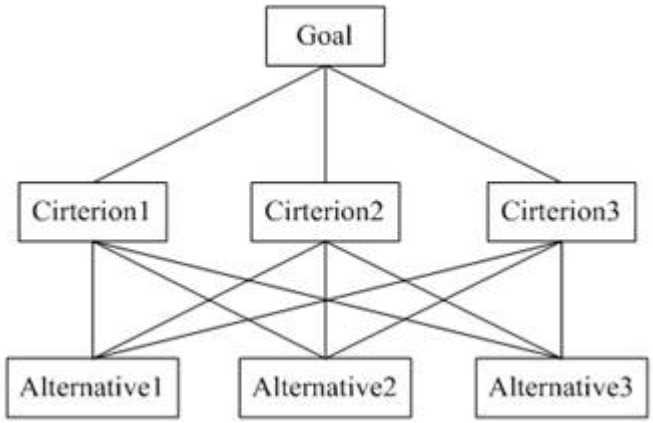
	NB	AG	GY	RANK
NB	1	3	1/3	24.3
AG	1/3	1	7	8.8
GY			1	66.9

(3x3) pairwise comparison matrix, n = 3

NB x AG: **3** Someone likes (**weakly more**) NB than AG
NB x GY : **1/3** Someone likes (**weakly more**) GY than NB
AG x GY: **7** Someone likes (**very strongly more**) AG than GY

Building a block diagram: risk assessment of carbon nanomaterials

Multicriteria method: AHP (Analytical Hierarchy Process)



Education	Tom	Dick	Harry	Priority
Tom	1	3	1/5	0.188
Dick	1/3	1	1/7	0.081
Harry	5	7	1	0.731
			Sum of Priorities	1.000
			Inconsistency	0.062

Control Banding (Risk assessment)

Environmental Hazard	Release Probability: Unlikely (1)	Low (2)	Likely(3)	Probable (4)
Very High or Unknown (D)	Control Level III	Control Level III	Control Level IV	Control Level IV
High (C)	Control Level II	Control Level II	Control Level III	Control Level IV
Medium (B)	Control Level I	Control Level I	Control Level II	Control Level III
Low (A)	Control Level I	Control Level I	Control Level I	Control Level II

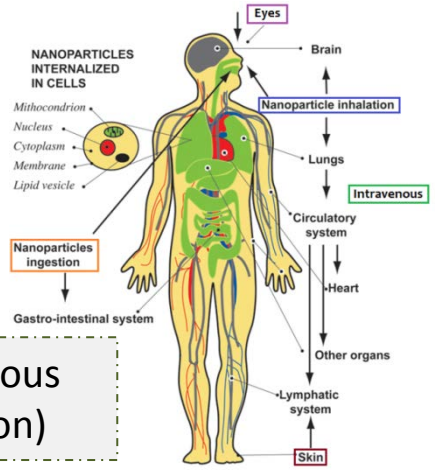
High quality (auditable) and simple as possible (not simpler) risk assessment model/tool.

AHP & CB: nanocarbons

Goal

Hazard Evaluation of Nanocarbons

Structuring the hierarchy:



Inhalation (Pulmonary) (Gast. Tract)

Dermal (Skin)

Ingestion (food/water)

ocular (air/skin)

Intravenous (injection)

Criteria

(workplace contamination route)

0D | 1D | 2D | 3D

Alternatives

Fullerenes (Quantum dots)

Carbon Nanotubes and nanofibres

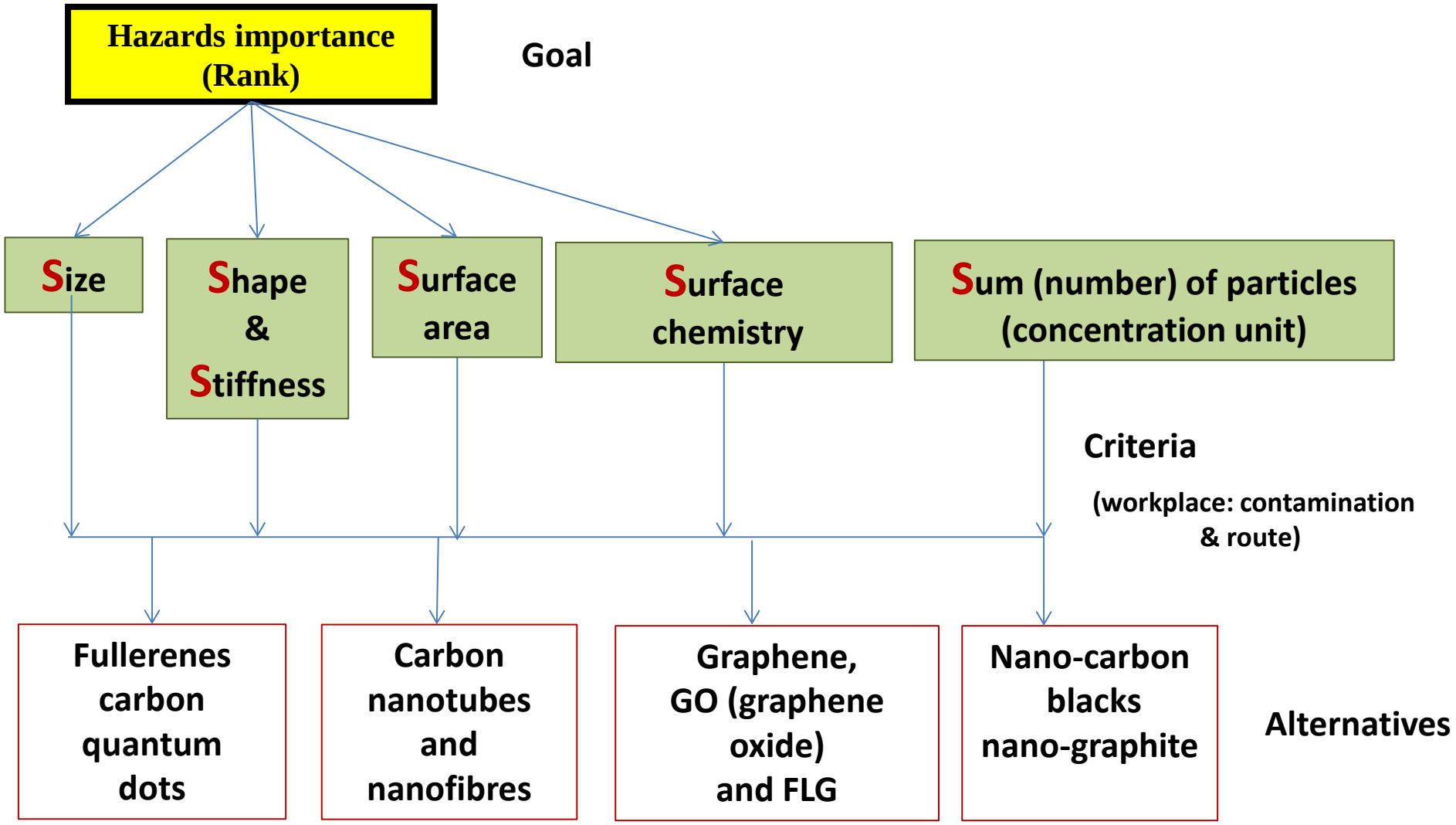
Graphene GO and FLG

Nano-carbon blacks nano-graphite

AHP pairwise comparison matrix example (workplace)

Cont. route	Inhalation	Dermal (Skin)	Ingestion	Ocular (eyes)	Intravenous	Rank (%)
Inhalation	1	4	7	6	9	**52.7**
Dermal	1/4	1	7	5	8	**25.5**
Ingestion	1/7	1/7	1	1/3	9	**8.1**
Ocular	1/6	1/5	3	1	9	**11.5**
Intravenous	1/9	1/8	1/9	1/9	1	**2.2**

Structuring a hierarchy:

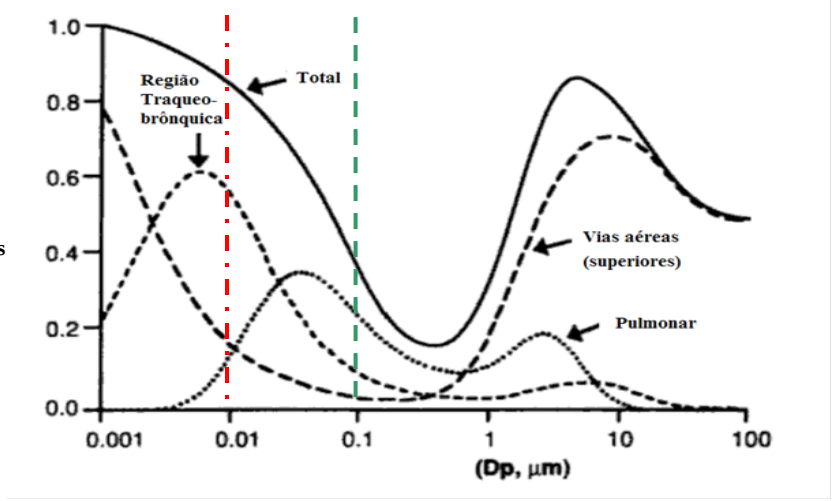


The "S" grouping multicriteria model.

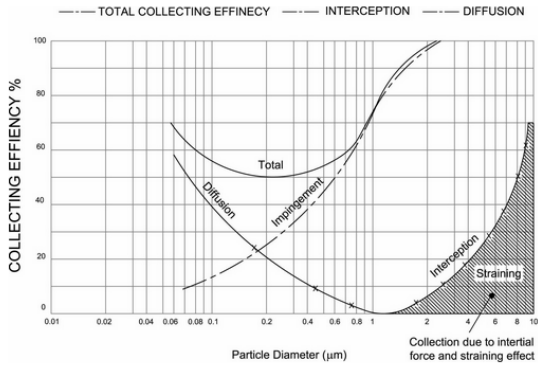
Size

Workplace ... If change the contamination pathway (like from food ingestion or medical treatment) ...

... A new rank will be necessary



Filtration collecting efficiency



http://www.tetisantesisat.com/air-filter-technology/air-filter-mechanisms

Size	<10 nm	10-100 nm	100-400 nm	400-1000 nm	>1000 nm	RANK (%)
<10 nm (TB), (AR) +(NPLR)	1	4	1/3	4	6	**27.5**
10-100 nm (NPLR)		1	1/5	3	5	**13.0**
100-400 nm			1	5	7	**48.1**
400 -1,000 nm				1	3	**7.6**
>1,000 nm					1	**3.8**

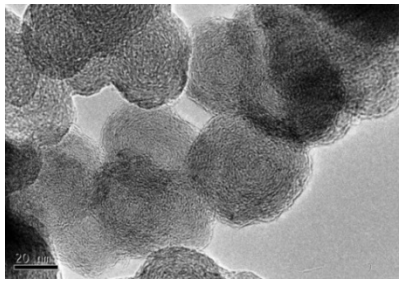
TB: tracheobronchial ; AR: alveolar region; NPLR: nasopharyngeal-laryngeal region.

Cell interaction with nanoparticles: the shape, size and stiffness aspects

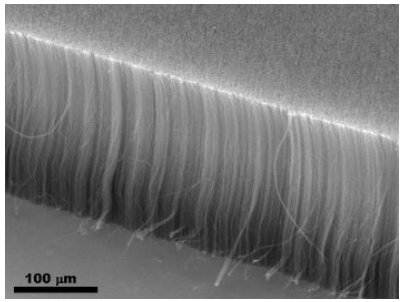
Carbon Materials:

Dimension	Size	Shape	Stiffness	Examples
0D	Nano	Spherical	Low to high	Carbon dots (*) Typically < 10 nm size materials
1D	Nano-millimeters	Linear Aligned (Cylindrical) bundles Spherical	High	Carbon Nanotubes (SWCNT, DWCNT, MWCNT) Carbon Fibers
2D	Nano-millimeters	Planar	Super-High	Graphene
3D	Nano-millimeters	Spherical, plates, etc.	Low to high	Nano-Graphite Nano-Carbon blacks

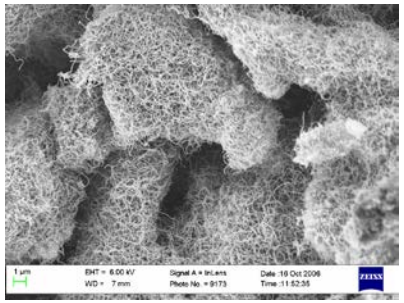
Size, Shape and Stiffness & Cells



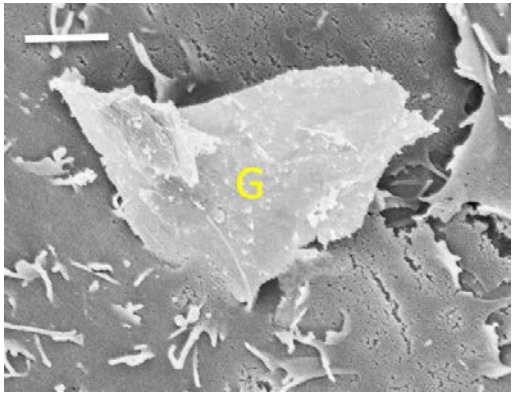
http://www.intechopen.com/books/modern-surface-engineering-treatments/coating-technology-of-nuclear-fuel-kernels-a-multiscale-view



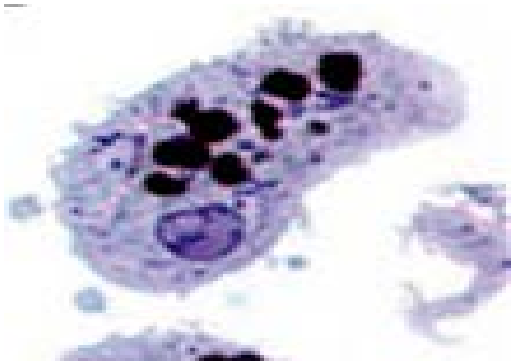
https://www.beilstein-journals.org/bjnano/single/articleFullText.htm?publicId=2190-4286-4-14&vt=f&sso=C&tpn=2&bpn=authors



Cell x nanoparticle interaction

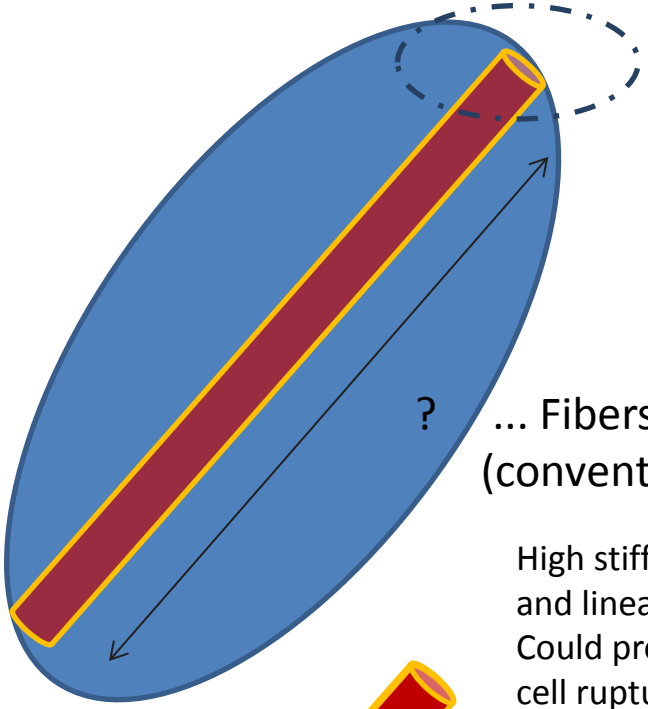


http://www.gizmag.com/graphene-bad-for-environment-toxic-for-humans/31851/



http://journals.cambridge.org/action/displayFulltext?type=6&fid=8753679&jid=MRS&volumeId=37&issueId=12&aid=8753678&bodyId=&membershipNumber=&societyETOCSession=&fulltextType=RA&fileId=S0883769412001819#cjofig_fig4

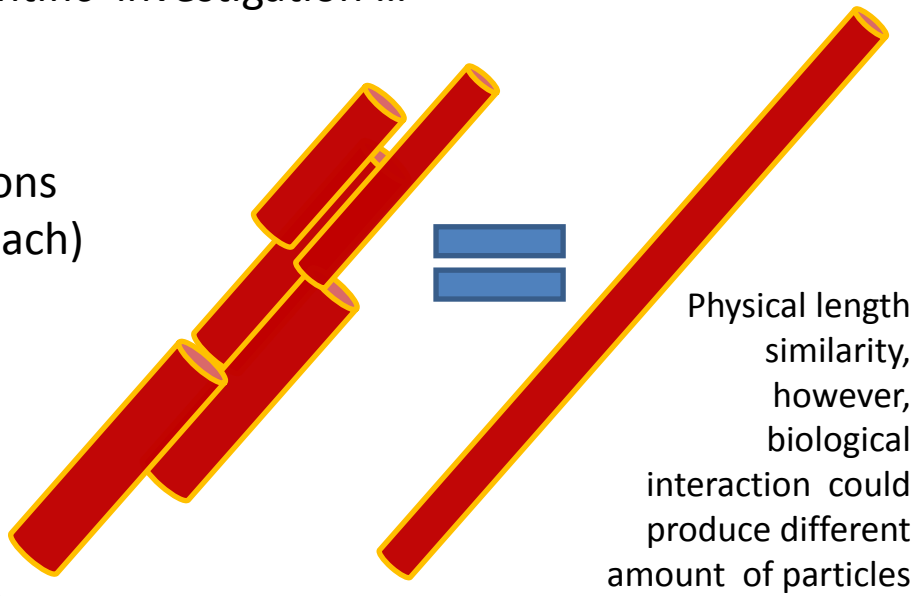
Intrinsic materials properties and cell interaction need more scientific investigation …



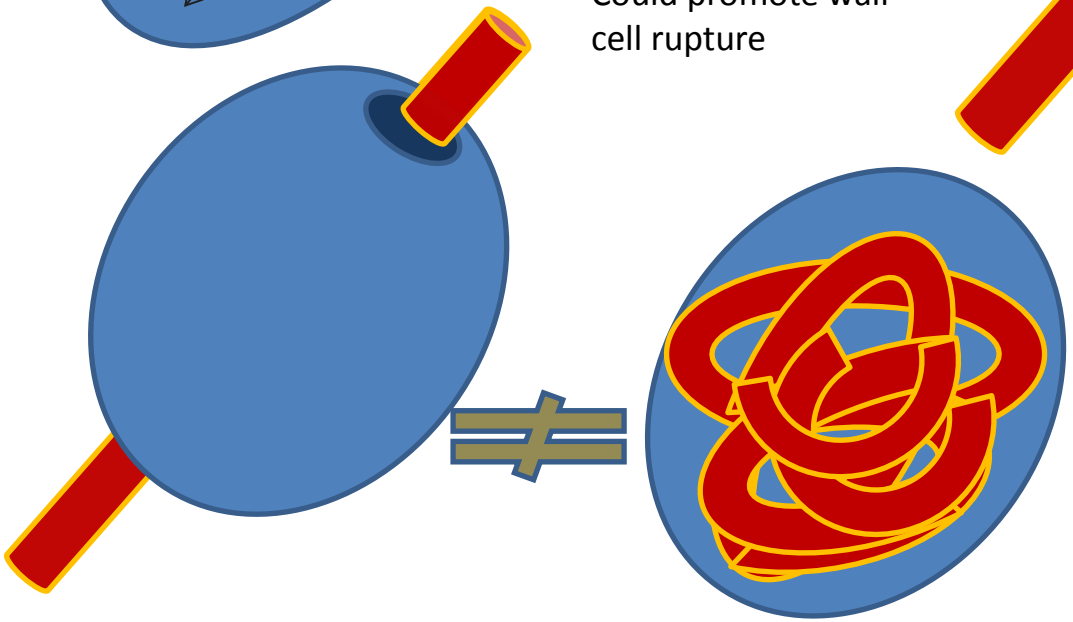
?

… Fibers: > 15 microns (conventional approach)

High stiffness and linear geometry: Could promote wall cell rupture

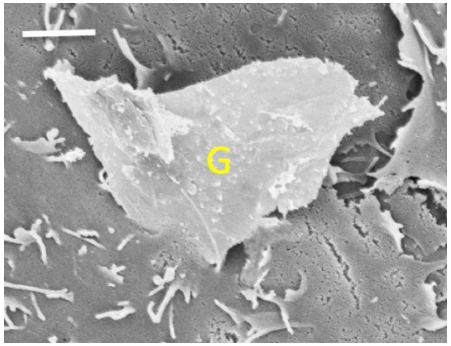


Physical length similarity, however, biological interaction could produce different amount of particles (by splitting of fibers or de-agglomeration process) and different toxicological response.



Shape: same length, same stiffness
but different shape/symmetry … Promote a different biological response (frustrated phagocytosis).

Shape



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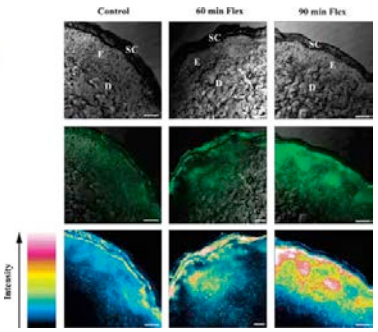
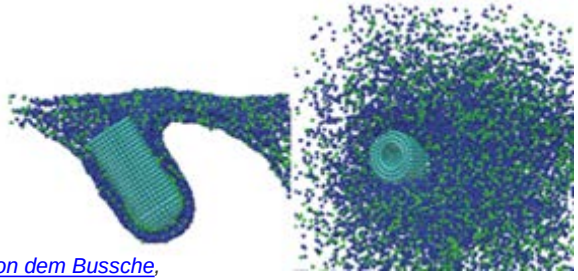


http://www.nanowerk.com/spotlight/spotid=1210.php

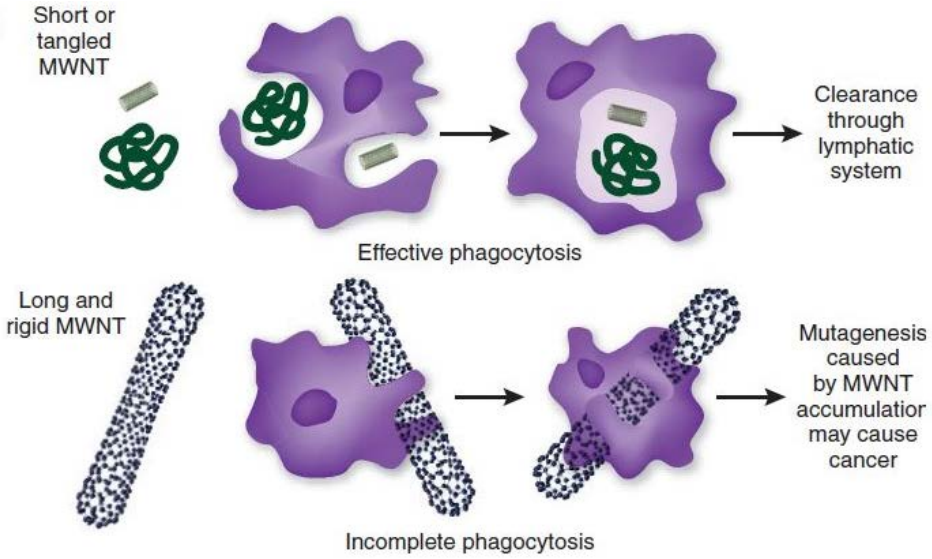
0D 1D 2D 3D

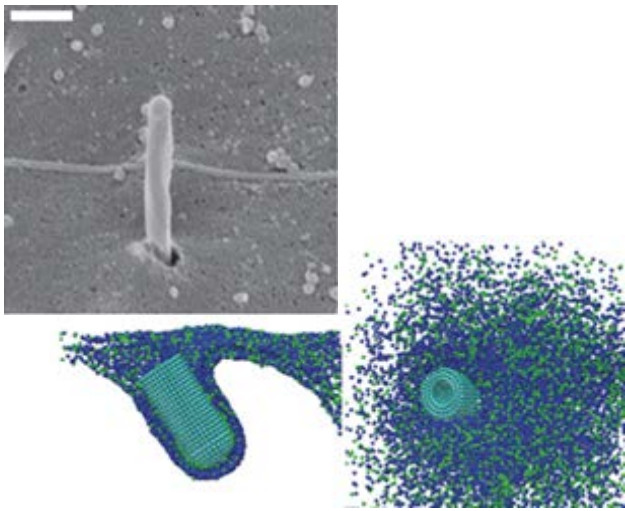
Aligned Non-Aligned



Xinghua Shi, Annette von dem Bussche, •Robert H. Hurt, Agnes B. Kane & Huajian Gao *Nature Nanotechnology*, 6, 714–719, (2011).

Shape	0D	1D (aligned)	1D (non-aligned)	2D	3D	Rank (%)
0D	1	1/7	1/3	1/3	6	**8.3**
1D (Aligned)		1	6	7	8	**62.2**
1D (Non-Aligned)			1	2	1/2	**11.5**
2D				1	4	**12.8**
3D					1	**5.3**



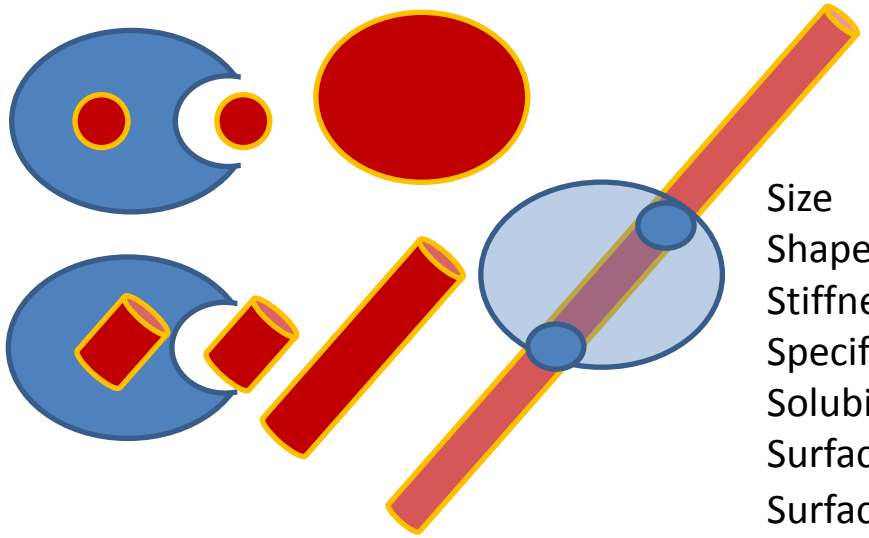


VOLUME 26 NUMBER 7 JULY 2008 NATURE BIOTECHNOLOGY

The long and short of carbon nanotube toxicity

Kostas Kostarelos

Xinghua Shi, Annette von dem Bussche, •Robert H. Hurt, Agnes B. Kane & Huajian Gao
Nature Nanotechnology, 6, 714–719, (2011).



Size
Shape
Stiffness
Specific chemical groups
Solubility
Surface area
Surface electric charge, ...

A better understanding of material properties and cell interaction is a very important aspect to predict toxicity of cells.

	Size	Shape	Surface area	Surface chemistry	Sum of particles (concentration unit)	Rank (%)
Size	**1**	X_1	X_2	X_3	X_4	K_1
Shape	$1/X_1$	**1**	Y_2	Y_3	Y_4	K_2
Surface area	$1/X_2$	$1/Y_2$	**1**	Z_3	Z_4	K_3
Surface chemistry	$1/X_3$	$1/Y_3$	$1/Z_3$	**1**	W_4	K_4
Sum of particles (concentration unit) (*)	$1/X_4$	$1/Y_4$	$1/Z_4$	$1/W_4$	**1**	K_5

(*) e.g. mass/m^2; mass/m^3 , number of particles/h , etc.

Decrease bias:

- Multicultural
- Multidisciplinary
- Worldwide participation
- Sample size, etc.

Numerical values	Verbal judgement of preferences
1	equally important
3	weakly more important
5	strongly more important
7	very strongly more important
9	absolutely more important

Surface chemistry	Amount of oxygen (%)	Solubility	State of aggregation	ROS (Reactive Oxygen Species)	Rank (%)
Amount of oxygen (%)	**1**	X_1	X_2	X_3	K_1
Solubility	$1/X_1$	**1**	Y_2	Y_3	K_2
State of aggregation	$1/X_2$	$1/Y_2$	**1**	Z_3	K_3
ROS (Reactive Oxygen Species)	$1/X_3$	$1/Y_3$	$1/Z_3$	**1**	K_4

Decrease bias:

- Multicultural
- Multidisciplinary
- Worldwide participation
- Sample size, etc.

Numerical values	Verbal judgement of preferences
1	equally important
3	weakly more important
5	strongly more important
7	very strongly more important
9	absolutely more important

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New tools to improve risk assessment of carbon nanoparticles.

HSEnano Health, Safety and Environment

HSEnano:

Provide good, free access, reliable information and guidance.

CONCLUSIONS

Building and using multicriteria decision tools based on AHP and CB could provide a new way to evaluate and improve the quality of risk assessment of nanomaterials, also it could:

- Improve the safety approach of laboratory and industry procedures;
- Help on design safer products and processes with a structured decisions strategy;
- Make/build a ranking of different types of nanocarbons (and confirm this ranking supported by previous toxicological studies or new studies);
- Integrate safety ranking with toxicological data from different nano raw materials;
- Integrate different and multiple point of view from worldwide participants using web-platforms;

CONCLUSIONS (Cont.)

-The sample size and expert judgment is a crucial point to incorporate different backgrounds and perspectives;
-Systematic studies covering intrinsic mechanical properties of different carbon nanotubes and physic-chemical properties such as length, aspect ration, shape, surface chemistry, stiffness, etc. must be done to improve the boundary conditions of risk assessment models;
-Worldwide participation is mandatory to decrease bias issues of decision model and create better mulicriteria risk assessment.

- Get involved !!!

- We would like to invite you to participate in this project.

- Please answer the survey and help us to improve the multicriteria risk assessment model and send us suggestions and comments !

Thanks
Aloha
Merci
Gracias
谢谢
Danke
Grazie
Teşekkürler
Obrigado

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