Qualitative and quantitative predictions of environmental exposure to nanomaterials from nanowaste streams

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4th International Conference on Nanotechnology – Occupational and Environmental Health (NANOEH09)

26- 29 August, 2009, Paasitorni, Helsinki, Finland

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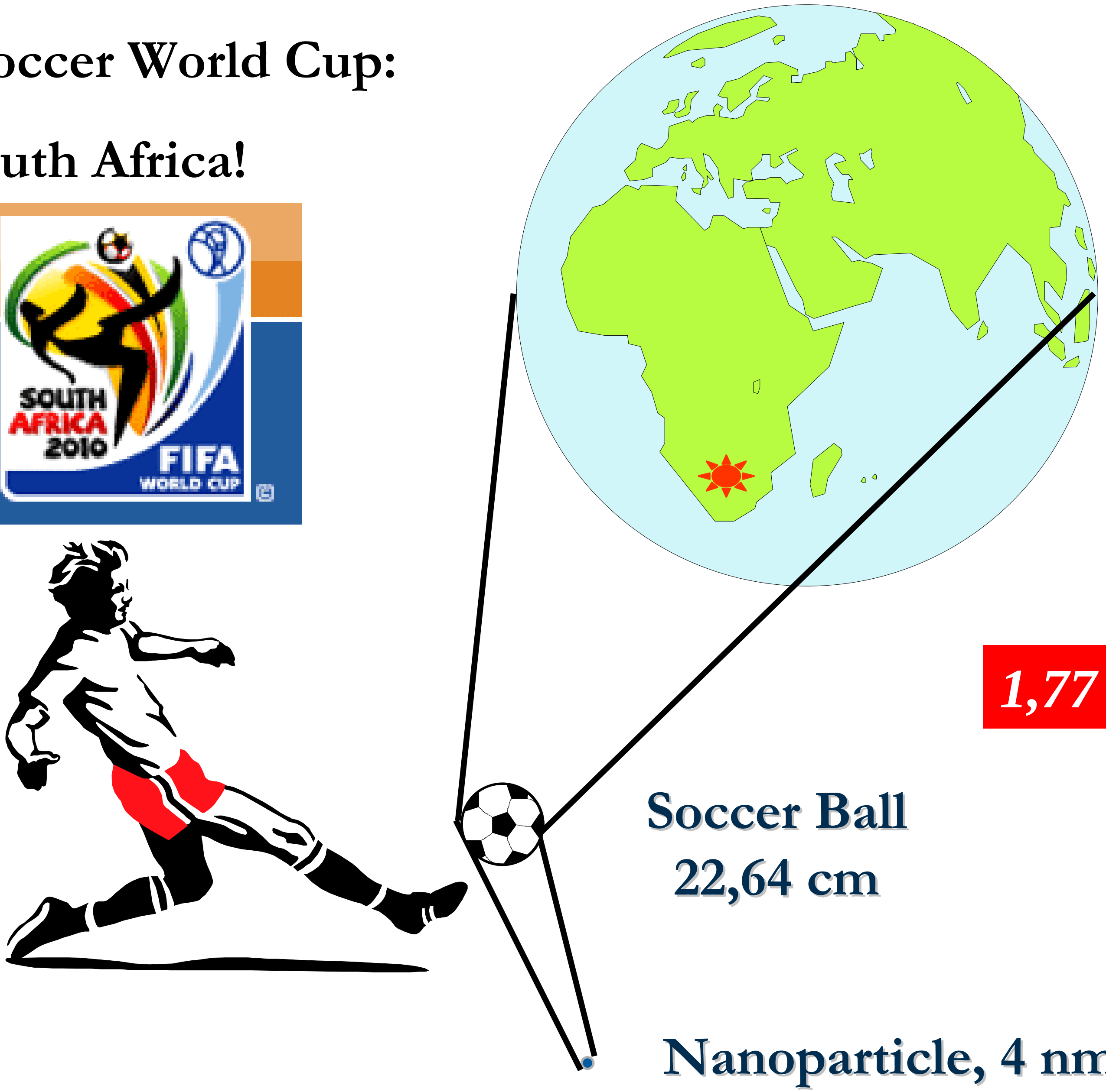
2010 Soccer World Cup:

South Africa!



Earth
12756 km

1,77 x 10^{-8} fold

Soccer Ball
22,64 cm

Nanoparticle, 4 nm

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Ideal environmental conditions… how do NMs behave here?

Why Nanowastes Now?

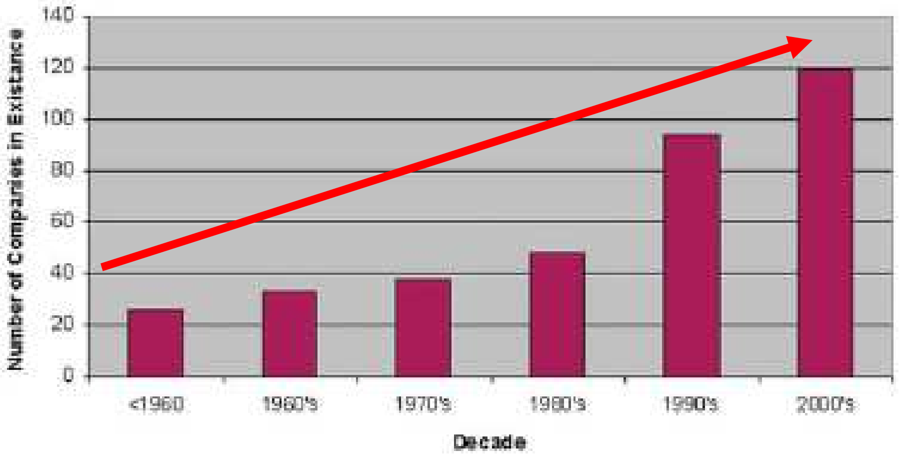
- Most probable vehicle of introducing NMs into the environment
- Current numerous waste management problems with macroscale chemicals/pollutants, and NMs may exacerbate the problem
- Janus-faced character of NMs: what makes them novel may generate a new/unique challenges to the waste management
- Absence of scientific data to elucidate the capabilities/effectiveness of the current waste management systems to deal with nanowaste streams adequately – **assumed to be effective** – **though no scientific proof**

QUESTION: Is it probable that treatment technologies developed without taking into account the novel nanoscale properties can prove to be efficient and effective for handling, storing, transporting, treating, and disposing nanowaste streams? **Most unlikely…**

- **Is there evidence of increasing quantities of nanowaste streams into the environment?**
- **Are there published quantities presently?**

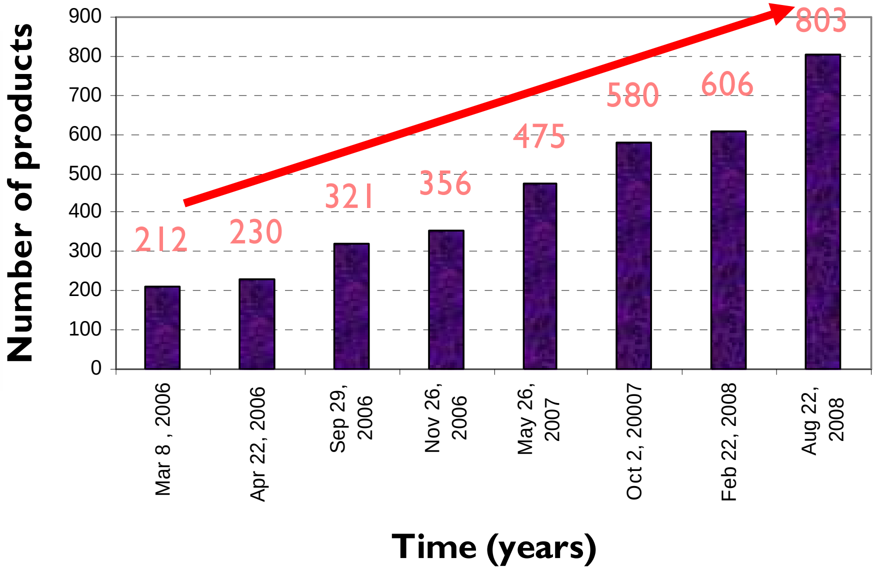
Company and Nanoproducts Growth

A



Global growth of companies fabricating NMs
(Pitkethly, 2003)

B



Consumer nanoproducts (Woodrow Wilson International Centre for Scholars, 2008)

Comment: Trend for nanowastes generation is obvious

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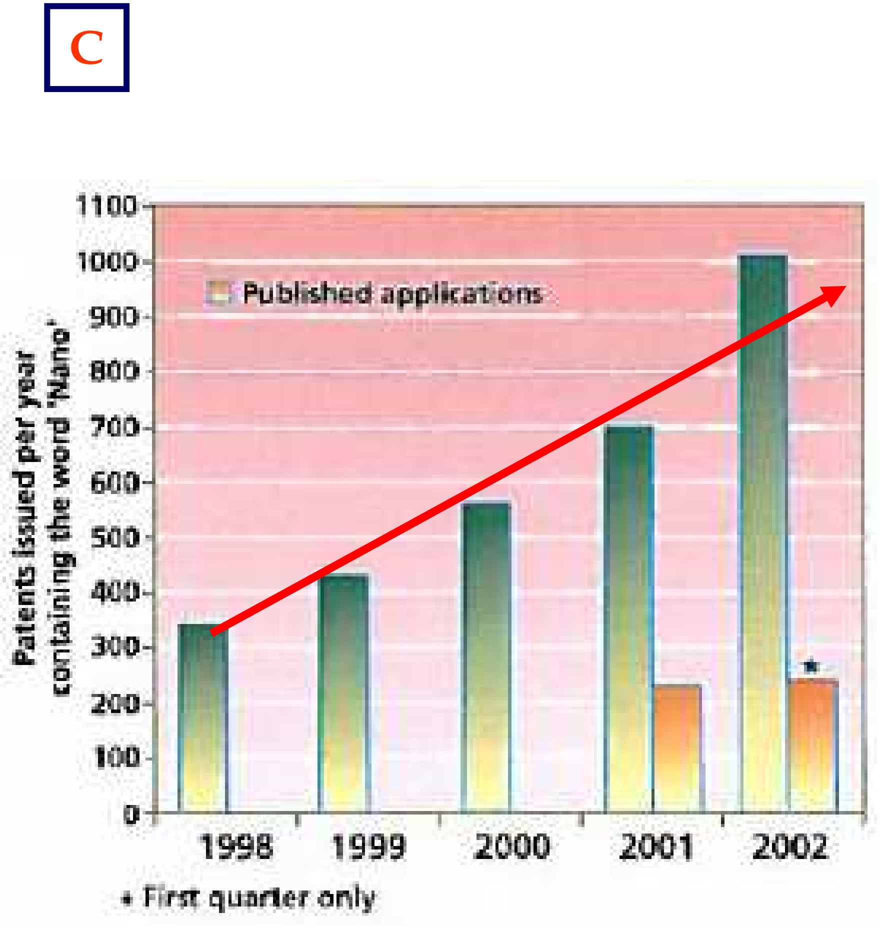
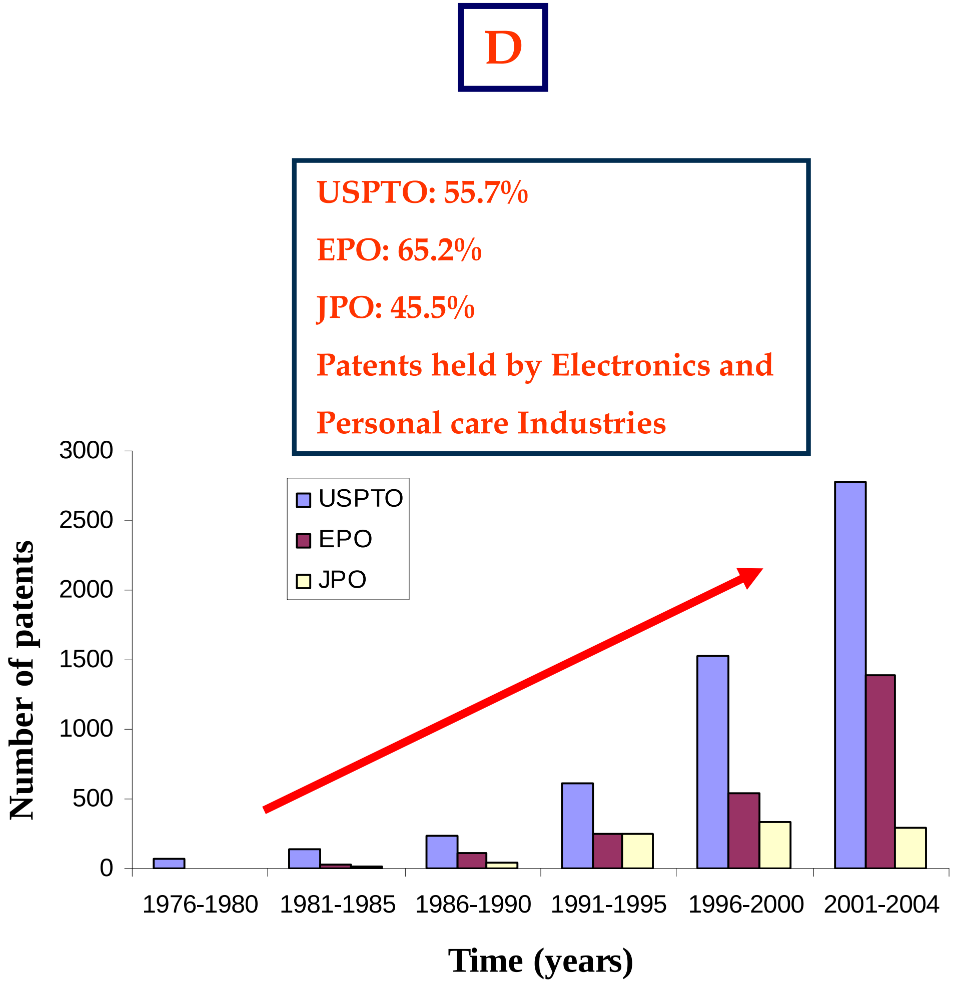
Growth of Nano-related Patents



Paull et al., Investing in nanotechnology, Nat Biotechnol 2003;21(10), 1144–1147..

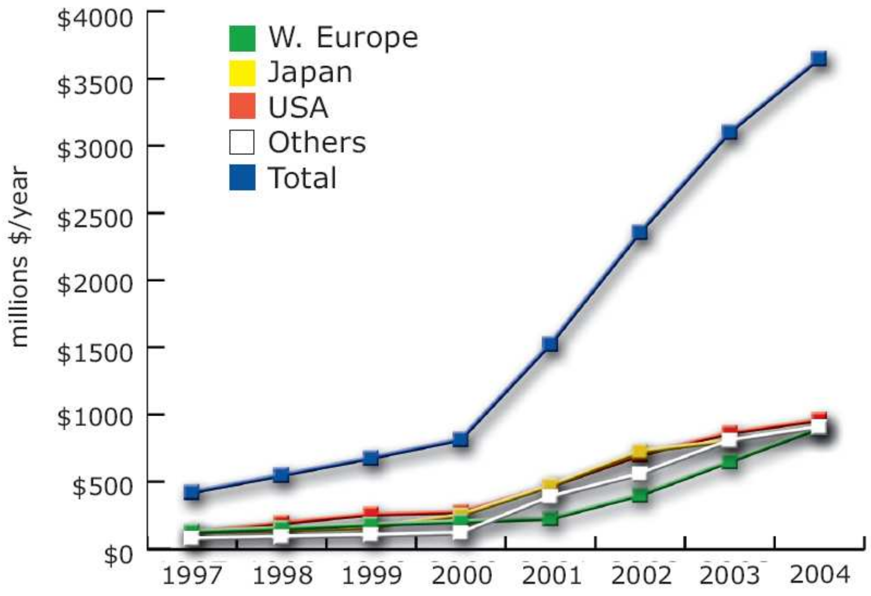


Nano-related IPs (Li et al., 2007; Huang et al.,2004)

Comment: Trend for nanowastes generation is obvious

Global Nano R&D and Venture Capital

E



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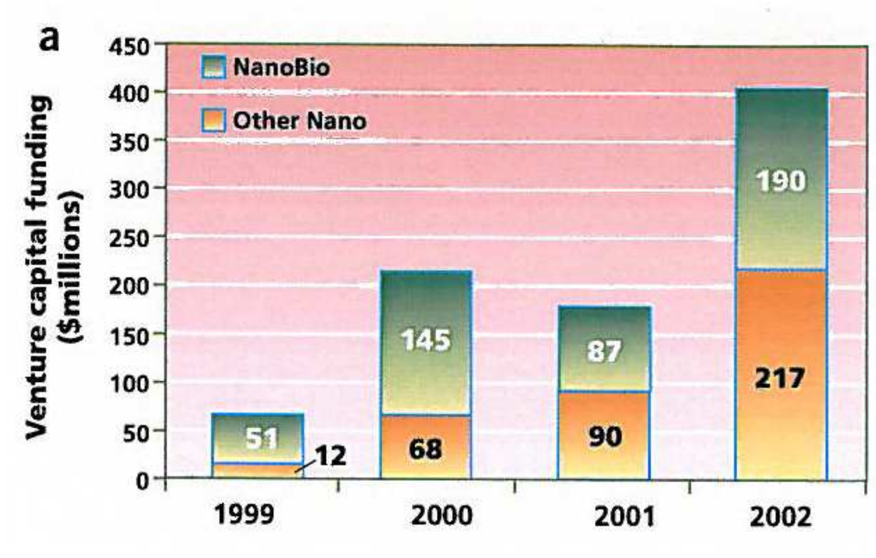


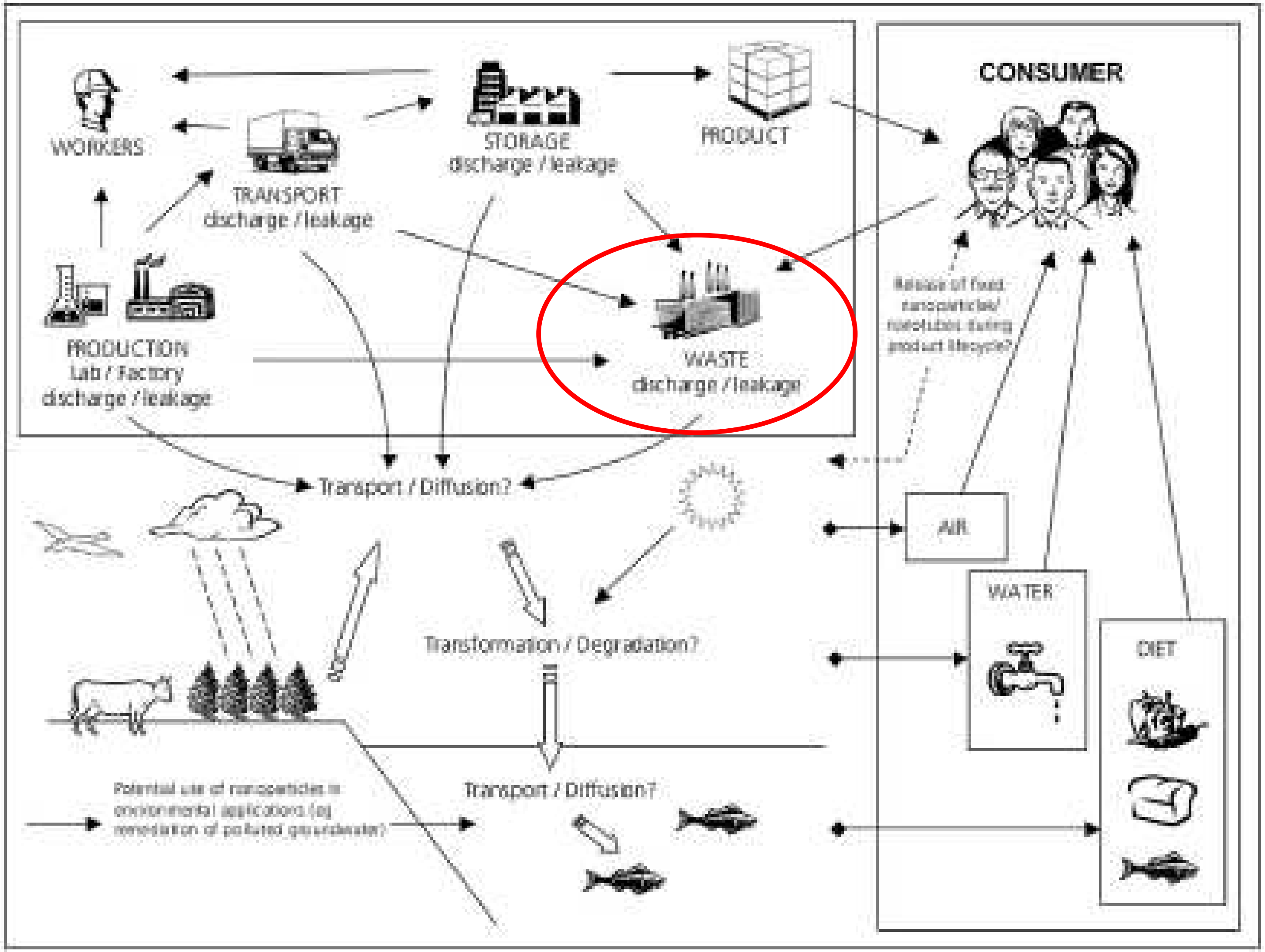
- **Currently less than 1% on SHE aspects**
- **Recommended level ca. 10%**
- **South Africa – no funding yet**

Paull et al., Investing in nanotechnology, Nat Biotechnol 2003;21(10), 1144–1147..

Source: M.C. Roco. 2004. ***Nanoscale Science and Engineering: Unifying and Transforming Tools.*** **AIChE Journal, Vol. 50, Issue 5, pp. 890-897.**

Comment: Trend for nanowastes generation is obvious

Exposure Pathways from Nanowastes



Source: Royal Society and Royal Academy of Engineering Report on Nanotechnology (2004)

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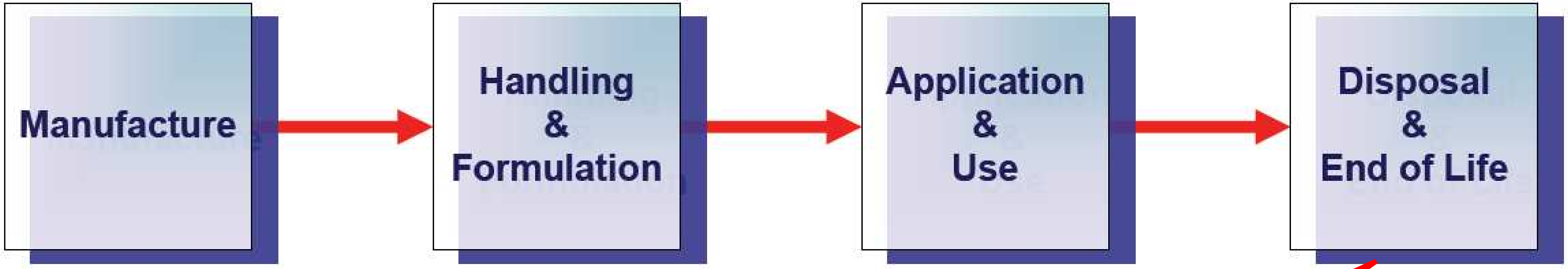
Risk Assessment of NMs in Nanoproducts


Manufacture

Handling
&
Formulation

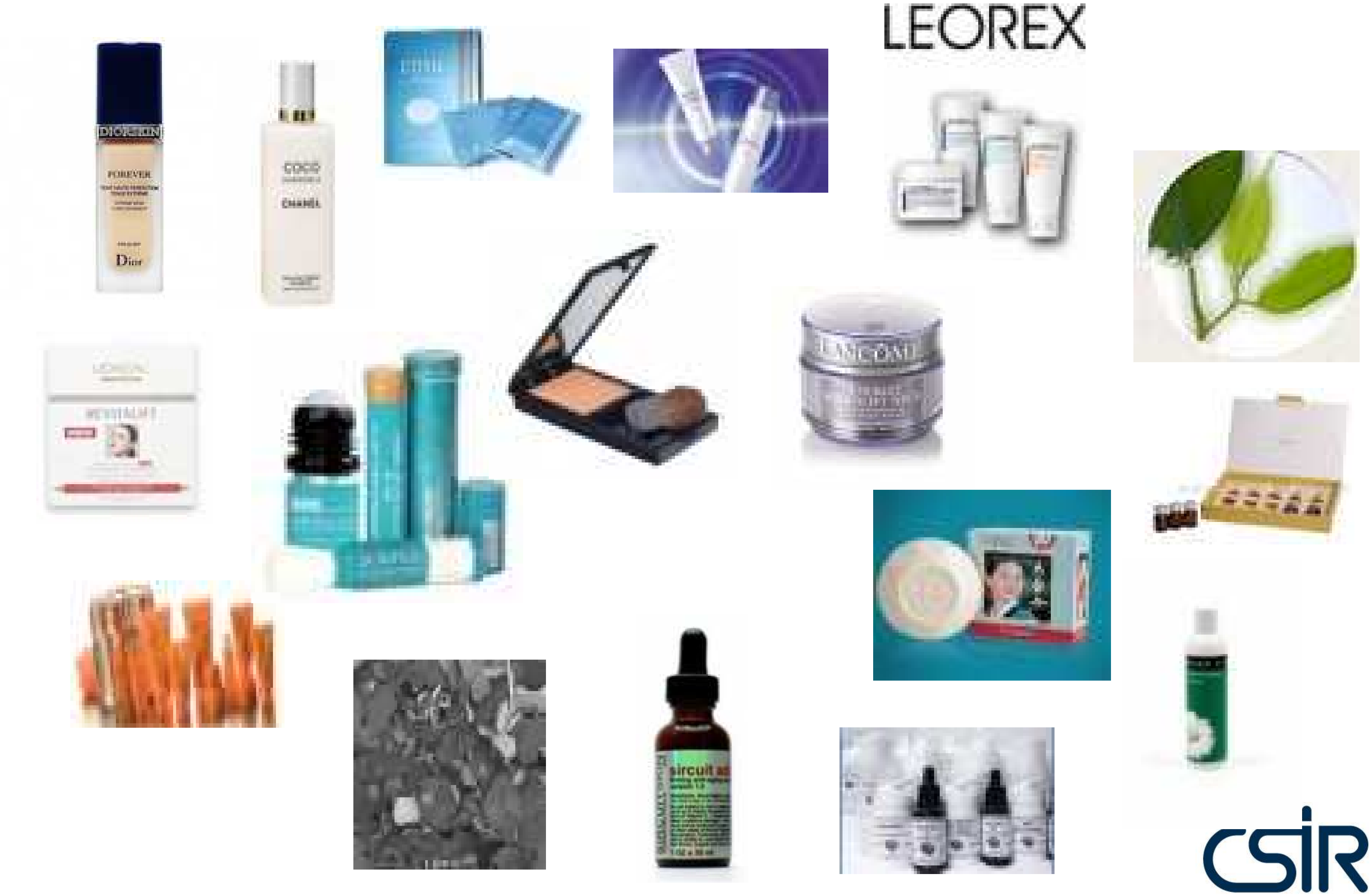
Application
&
Use

Disposal
&
End of Life

Life cycle stage	Aquatic and soil organisms	Humans	No evaluation	Missing
Production Site	2.5% (n = 1)	5.0% (n = 2)	75.0% (n = 30)	17.5% (n = 7)
Finished product	2.5% (n = 1)	5.0% (n = 2)	77.5% (n = 31)	15.0% (n = 6)
Disposal	0	0	82.5% (n = 33)	17.5% (n = 7)

Helland et al., Environ. Sci. Technol., 2008;42(2):640-646

Just Few Cosmetic Products…



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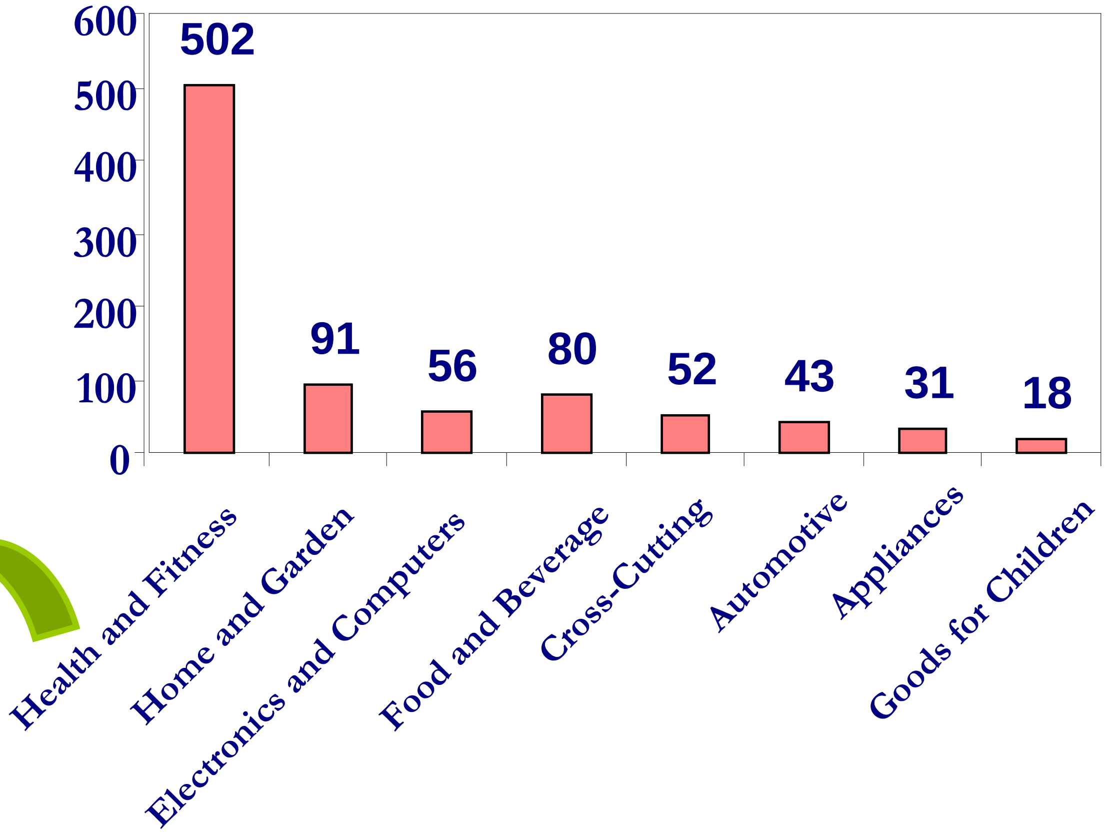
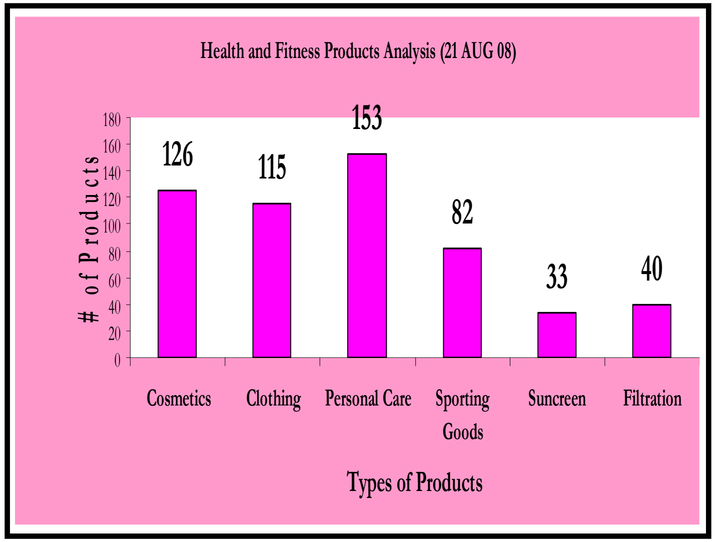
Cosmetics Products





Source: Woodrow Wilson International Centre for Scholars, 2009

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Qualitative Model

What likely classes of nanowastes are we likely to encounter presently and coming years?

Qualitative risk assessment of nanowastes

- **Risk is a function of anticipated hazard and exposure potency**

  - Expected hazard (toxicity) owing to constituent NMs (end-points results of *Bacillus subtilis, Daphnia magna, Oncorhynchus mykiss, P. subsapiata, Micropterus salmoides, etc)*

  - Likelihood of exposure (normally computed using bioaccumulation and biopersistence) – loci of NMs in products/applications is currently applied as exposure potency computed suing bioaccumulation and persistence is currently unavailable.

Qualitative quantification of toxicity levels

NMs type	Examples	Hazard (toxicity)[1]
Carbon based	Fullerenes	High
	Singled-walled carbon nanotubes (SWCNT)	High
	Multi-walled carbon nanotubes (MWCNT)	High
Metal oxides	Zinc oxide (ZnO)	Medium
	Titanium oxide (TiO_2)	Low
	Aluminium oxide (Al_2O_3)	Medium
	Yttrium iron oxide ($Y_3Fe_5O_{12}$)	Low
	Silicon dioxide (SiO_2)	Low
	Iron oxide (Fe_2O_3)	Medium
Metals	Silver (Ag)	Medium
	Gold (Au)	High
	Silica (Si)	Low
Quantum dots	Cadmium-selenide (CdSe)	High
	Cadmium telluride (CdTe)	High
Others	Silicon nanowires	Low
	Nanoclay particles	Low
	Dendrimers	Medium

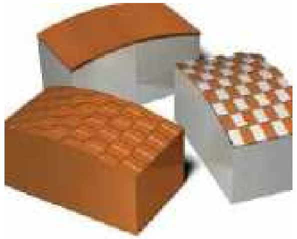
[1] Classification based on Globally Harmonized System (GHS, 2003; Silk, 2003) aquatic toxicity can be expressed in five classes namely; extremely toxic (<0.1 mg/l); very toxic (0.1-1 mg/l); toxic (1-10 mg/l); harmful (10-100 mg/l); and none toxic (>100 mg/l) which were reduced into the three classes (high, medium and low).

Exposure Potency: Loci of ENMs in Products

Bulk-based NMs

(one or multiphase)

EP: Very low to low



Structured surface, film or

Structured film

EP: Very low to medium

Surface bound

EP: Low to high

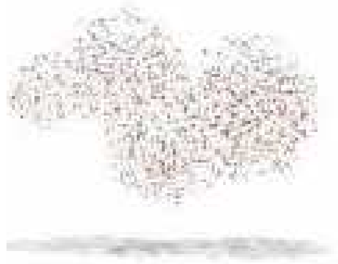
NMs suspended

in liquids

EP: Highly likely

NMs suspended in solids

EP: Medium to very high



Airborne/free ENPs

EP: Highly likely

Nanomaterials classification framework (Hansen et al. 2007)

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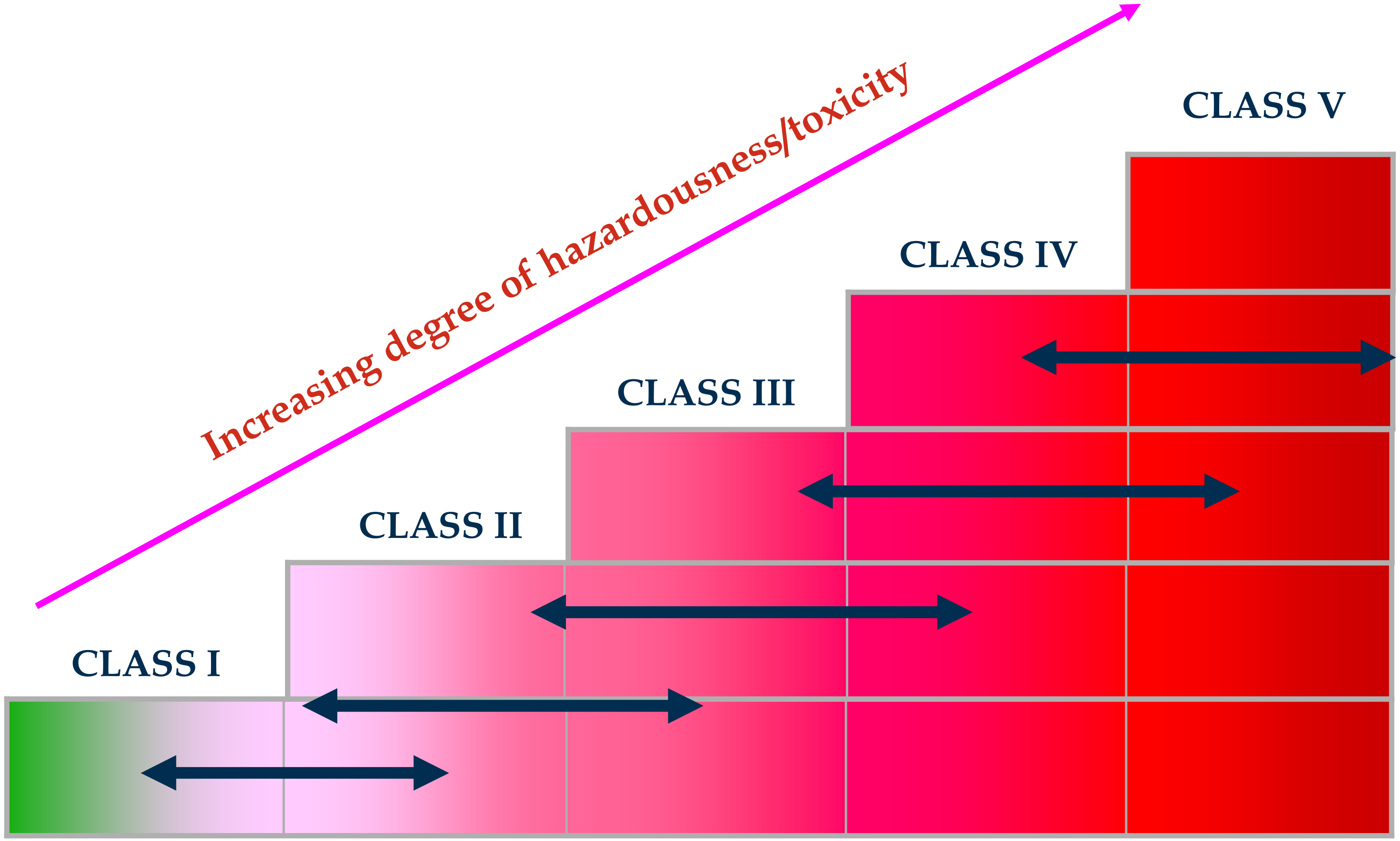
Pictorial nanowaste classification



- **Benign**
- **Minimum cost**

- **Extremely toxic**
- **Very expensive**

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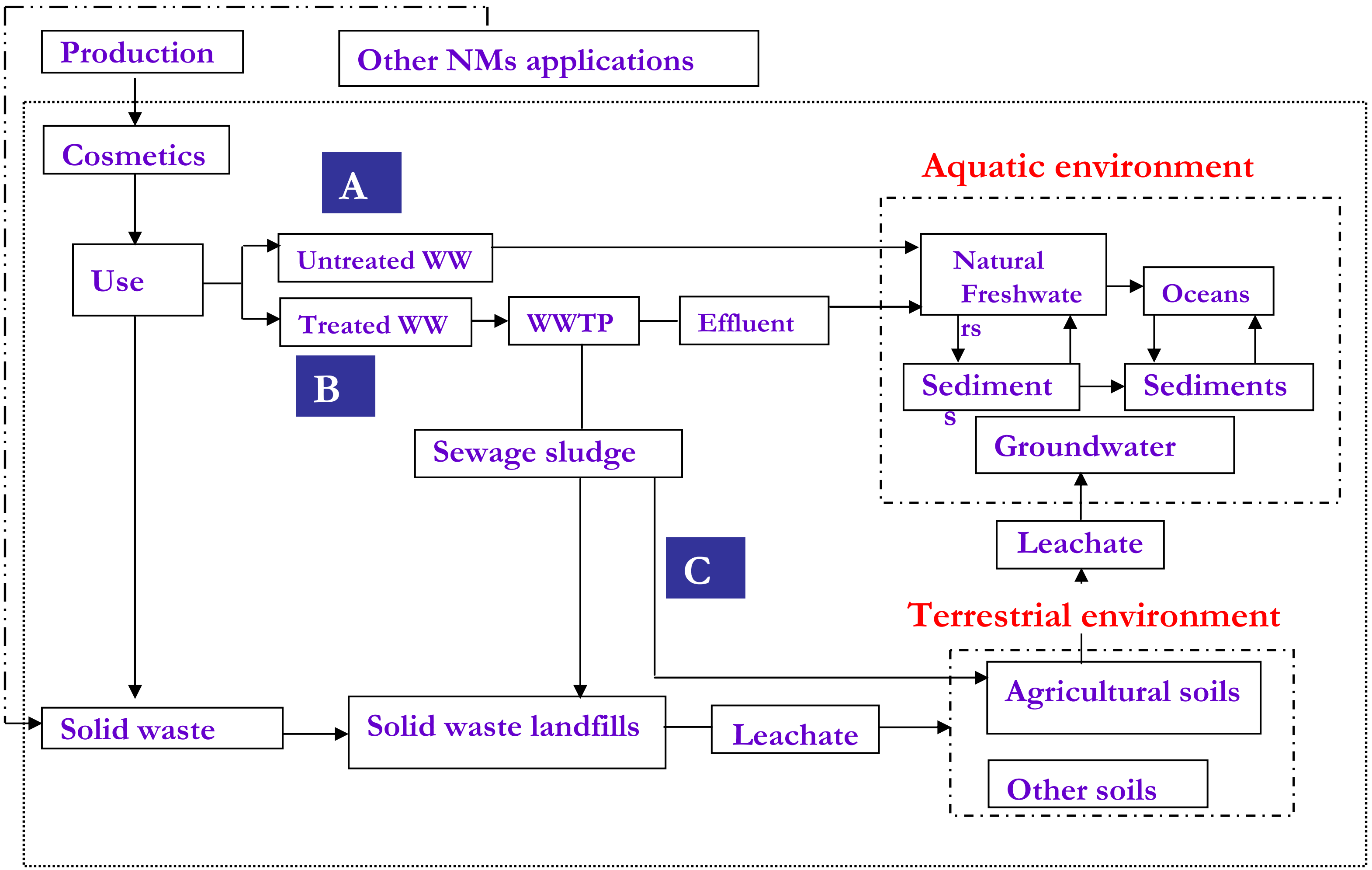
Quantitative Model

What quantities of nanomaterials will result into the environment from nanoproducts?

Case of Johannesburg in SA

Probable Environmental NMs flows in SA Scenario



Production

Other NMs applications

Cosmetics

A

Aquatic environment

Use

Untreated WW

Treated WW

WWTP

Effluent

B

Natural Freshwaters

Oceans

Sediments

Sediments

Groundwater

Sewage sludge

C

Leachate

Terrestrial environment

Agricultural soils

Solid waste

Solid waste landfills

Leachate

Other soils

System boundary

NMs flow in cosmetics

NMs flow in cosmetics

Environmental compartments

WWTP: wastewater treatment plant

WW: wastewater

Quantitative Risk Assessment of NMs in Environment

- Computation of the predicted environmental concentrations (PEC)
- Determination of predicted no effect concentration (PNEC)
- Risk profile of a given NM pollutant

$$RQ = \frac{PEC_{NMi}}{PNEC_{NMi}}$$

RQ: Risk Quotient

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Case Study: City of Johannesburg

Quantities of NM in JHB computed based on the expression:

$$JHB_{NM} = SW_{NM} \bullet cf_1 \bullet cf_2 \bullet cf_3 \bullet \frac{GDP_{JHB}}{GDP_{SA}}$$

cf: correction factor

$cf_1 = \frac{POP_{SA}}{POP_{SW}}$:Population ratio of SA to SW

$cf_2 = \frac{GDP / capita(SA)}{GDP / capita(SW)}$: GDP ratio of SA to SW (0.391) -2007

$cf_3 = Market - penetration$: 3 scenarios (0.1, 0.25, 0.40)

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Total NMs into Aquatic Environment

$$NM_{Water,input\,i} = NM_{WW,Total\,i} \bullet (1 - f_{STPi}) + NM_{WW,Total\,i}(f_{STPi} - f_{STPi} \bullet f_{\mathrm{Re}moval\,i})$$

Untreated wastewater

A

Treated wastewater (effluent)

B

$$NM_{Water,input\,i} = NM_{WW,Total\,i} \bullet (1 - f_{STPi} \bullet f_{\mathrm{Re}moval\,i})$$

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Calculation of C_{STPs}, PECs & PNECs

$$C_{WW} = C_{STP} = \frac{NM_{i,WW,STP} \times 10^{12}}{WW_{percapita} \bullet f_{STP} \bullet POP}$$

$$PEC_i = \frac{NM_{i,Water} \bullet 10^{12}}{POP \bullet WW_{percapita} \bullet D_k} = C_{STP} \bullet \frac{NM_{i,Water}}{NM_{i,WW,STP}} \bullet \frac{f_{STP}}{D_k}$$

PNECs derived from the literature: 40 & 1 ug/l for nAg and nTiO2, respectively

JHB WWTP (High Efficient Plants)

WWTP efficiency 20-30% less values reported by Westehoff et al., 2008

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NMs in JHB Aquatic Environment (Higher Eff)

	Variable	**MIN-E_{JHB}**	**PRO E_{JHB}**	**MAX E_{JHB}**
Ag	Ag_{total} : total silver released into WW (kg/a)	**7.77**	**52.79**	**306.58**
	: fraction of WW treated in WWTPs	0.80	0.70	0.60
	: fraction of Ag removed in WWTPs	0.79	0.70	0.55
	Ag_{STP}: silver entering into WWTPs in (kg/a)	6.22	36.95	183.95
	$Ag_{STP,removed}$: silver removed in WWTP (Ag in sludge) (kg/a)	4.91	25.87	101.17
	$Ag_{STP,removed}$: silver released effluents from WWTPs (kg/a)	3.93	11.09	82.78
	$Ag_{untreated}$: silver in untreated WW (kg/a)	1.55	15.84	122.63
	Ag_{water}: silver that enters into aquatic environment (kg/a)	**2.86**	**26.92**	**205.41**
TiO_2	$TiO2_{total}$: total TiO_2 released into WW (kg/a)	**7.03**	**47.73**	**1 289.38**
	: fraction of WW treated in WWTPs	0.80	0.70	0.60
	: fraction of TiO_2 removed in WWTPs	0.80	0.65	0.60
	TiO_{2STP}: TiO_2 entering into WWTPs in (kg/a)	5.62	33.41	773.63
	$TiO_{2STP,removed}$: TiO_2 removed in WWTP (Ag in sludge) (kg/a)	4.50	21.72	464.18
	$TiO_{2STP,removed}$: TiO_2released effluents from WWTPs (kg/a)	1.12	11.69	309.45
	$TiO_{2, untreated}$: TiO_2 in untreated WW (kg/a)	1.41	14.32	515.75
	TiO_{2water}: TiO_2 entering into the aquatic environment (kg/a)	**2.53**	**26.01**	**825.21**

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Quantitative RQs Results (Higher Eff)

	Parameters	MIN-E_{JHB}		PRO-E_{SW}		MAX-E_{SW}	
nAg	***Concentration in STP (µg/ℓ)***	4.8E-03	7.68E-03	36.28E-03	90.58E-03	23.268E-03	1038.48E-03
	Dilution factor: 10 (PEC, µg/ℓ)	0.2E-03	0.3E-03	1.8E-03	4.6E-03	15.6E-03	69.6E-03
	Dilution factor: 3 (PEC, µg/ℓ)	0.6E-03	0.9 E-03	6.2E-03	15.4 E-03	52E-03	231.9E-03
	Dilution factor: 1 (PEC, µg/ℓ)	1.8E-03	2.8E-03	18.5E-03	46.2E-03	155.9E-03	695.7E-03
	RQ (D=10) (no units)	4.44E-06	7.01E-06	4.62E-05	1.15E-04	3.90E-04	1.74E-03
	RQ (D=3) (no units)	1.48E-05	2.34E-05	1.54E-04	3.85E-04	1.30E-03	5.80E-03
	RQ (no dilution) (no units)	4.44E-05	7.01E-05	4.62E-04	1.15E-03	3.90E-03	1.74E-02
$nTiO_2$	***Concentration in STP (µg/ℓ)***	4.4E-03	6.9E-03	32.7E-03	81.8E-03	977.2E-03	4 361.9E-03
	Dilution factor: 10 (PEC, µg/ℓ)	0.2E-03	0.3E-03	1.8E-03	4.5E-03	62.5E-03	279.2E-03
	Dilution factor: 3 (PEC, µg/ℓ)	0.5E-03	0.8E-03	5.9E-03	14.9E-03	208.5E-03	930.5E-03
	Dilution factor: 1 (PEC, µg/ℓ)	1.6E-03	2.5E-03	17.8E-03	44.6E-03	625.4E-03	2 791.6E-03
	RQ (D=10) (no units)	1.57E-04	2.48E-04	1.78E-03	4.46E-03	6.25E-02	2.79E-01
	RQ (D=3) (no units)	5.24E-04	8.26E-04	5.95E-03	1.49E-02	2.08E-01	9.31E-01
	RQ (no dilution) (no units)	1.57E-03	2.48E-03	1.78E-02	4.46E-02	6.25E-01	2.79E+00

Under each scenario, first column results based on calculated WW per capita, and second column based on values provided by experts in WWT in SA

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JHB WWTP (Low Efficient Plants)

WWTP efficiency 25 – 40% values by experts in WW in SA

JHB WWTP (Low Efficient Plants)… cont…

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JHB WWTP (Low Efficient Plants)… cont…

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NMs in JHB Aquatic Environment (Lower Eff)

	Variable	**MIN-E$_{JHG}$**	**PROE$_{JHB}$**	**MAX-E$_{JHB}$**
nAg	Ag_{total} : total silver released into WW (kg/a)	**7.77**	**52.79**	**306.58**
	: fraction of WW treated in WWTPs	0.80	0.70	0.60
	: fraction of Ag removed in WWTPs	0.45	0.35	0.25
	Ag_{STP}: silver entering into WWTPs in (kg/a)	6.22	37.0	183.95
	$Ag_{STP,removed}$: silver removed in WWTP (Ag in sludge) (kg/a)	2.80	12.90	46.00
	$Ag_{STP,removed}$: silver released effluents from WWTPs (kg/a)	3.40	24.00	138.10
	$Ag_{untreated}$: silver in untreated WW (kg/a)	1.60	15.80	122.80
	Ag_{water}: silver that enters into aquatic environment (kg/a)	**5.00**	**39.90**	**260.90**
nTiO_2	$TiO2_{total}$: total TiO_2 released into WW (kg/a)	**7.03**	**47.73**	**1 289.38**
	: fraction of WW treated in WWTPs	0.80	0.70	0.60
	: fraction of TiO_2 removed in WWTPs	0.45	0.35	0.25
	TiO_{2STP}: TiO_2 entering into WWTPs in (kg/a)	5.60	33.40	773.60
	$TiO_{2STP,removed}$: TiO_2 removed in WWTP (Ag in sludge) (kg/a)	2.50	11.70	193.40
	$TiO_{2STP,removed}$: TiO_2released effluents from WWTPs (kg/a)	3.10	21.70	580.20
	$TiO_{2,\ untreated}$: TiO_2 in untreated WW (kg/a)	1.40	14.30	515.80
	TiO_{2water}: TiO_2 entering into the aquatic environment (kg/a)	**4.50**	**36.00**	**1 096.0**

Quantitative RQs Results (Lower Eff)

	Parameters	**MIN-E$_{\mathrm{JHG}}$**		**PRO-E$_{\mathrm{JHB}}$**		**MAX-E$_{\mathrm{JHB}}$**	
nAg	*Concentration in STP (µg/ℓ)*	4.8E-03	7.68E-03	36.28E-03	90.58E-03	23.268E-03	1038.48E-03
	Dilution factor: 10 (PEC, µg/ℓ)	0.3E-03	0.5E-03	2.7E-03	6.8E-03	19.8E-03	88.3E-03
	Dilution factor: 3 (PEC, µg/ℓ)	1.0E-03	1.6E-03	9.1E-03	22.8E-03	65.9E-03	294.2E-03
	Dilution factor: 1 (PEC, µg/ℓ)	3.1E-03	4.9E-03	27.3E-03	68.3E-03	197.7E-03	882.6E-03
	RQ (D=10) (no units)	7.72E-06	1.22E-05	6.83E-05	1.71E-04	4.94E-04	2.21E-03
	RQ (D=3) (no units)	2.57E-05	4.06E-05	2.28E-04	5.69E-04	1.65E-03	7.35E-03
	RQ (no dilution) (no units)	7.72E-05	1.22E-04	6.83E-04	1.71E-03	4.94E-03	2.21E-02
nTiO$_2$	*Concentration in STP (µg/ℓ)*	4.4E-03	6.9E-03	32.7E-03	81.8E-03	977.2E-03	4 361.9E-03
	Dilution factor: 10 (PEC, µg/ℓ)	0.3E-03	0.4E-03	2.5E-03	6.2E-03	83.1E-03	370.8E-03
	Dilution factor: 3 (PEC, µg/ℓ)	0.9E-03	1.5E-03	8.2E-03	20.6E-03	276.9E-03	1 235.9E-03
	Dilution factor: 1 (PEC, µg/ℓ)	2.8E-03	4.4E-03	24.7E-03	61.8E-03	830.6E-03	3 707.6E-03
	RQ (D=10) (no units)	2.79E-04	4.41E-04	2.47E-03	6.18E-03	8.31E-02	3.71E-01
	RQ (D=3) (no units)	9.31E-04	1.47E-03	8.24E-03	2.06E-02	2.77E-01	1.24E-00
	RQ (no dilution) (no units)	2.79E-03	4.41E-03	2.47E-02	6.18E-02	8.31E-01	3.71E+00

Under each scenario, first column results based on calculated WW per capita, and second column based on values provided by experts in WWT in SA

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Summary

- Waste-related issues have begun to challenge present waste management systems.

- Are the current systems adequate for dealing with them?

- Need for more focussed research to quantify the risks owing to these forms of waste streams is imperative, as well as the development of mechanisms to deal with them adequately.

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