Simple models for estimating nanomaterials accumulation in the environment: a case of JHB

Musee, N, Nota, N
Natural Resources and Environment, RSA

Bytes Business Park, Midrand, Johannesburg, South Africa, 2nd – 3rd September, 2009

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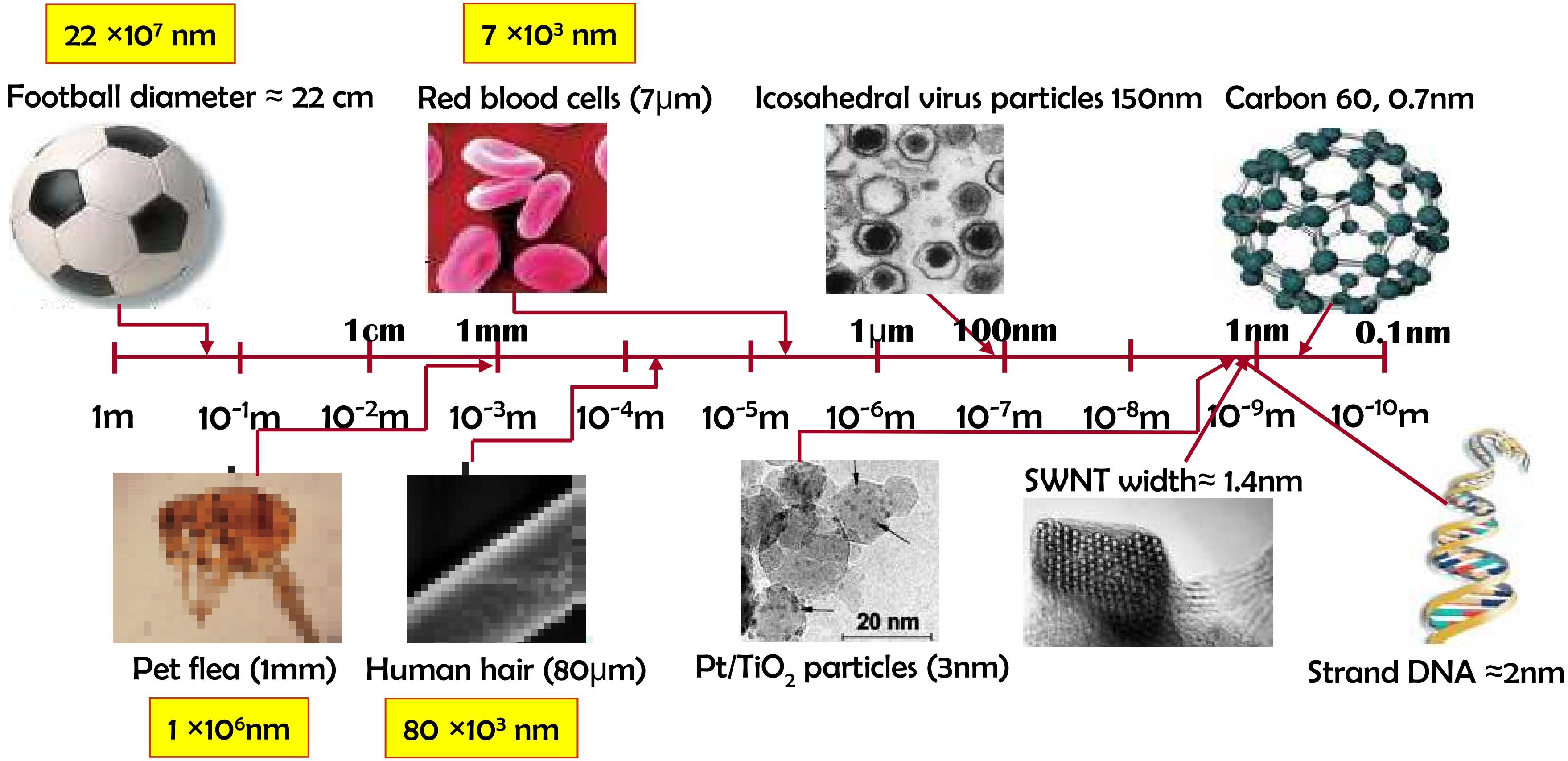
Nanotechnology: Course 101 (Introduction)



The ratio of one nanometre to the human head is equivalent to the diameter of human head to the earth's diameter

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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Nanotechnology applications and products…

X

But… are we sure we do know what happens when these materials and products enter into humans and the environment ????

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Nanotechnology Risk Concerns in South Africa

Example 1


The science of the tiny is big news

From medicine to media, this will revolutionise our lives

Nanotechnology proves problems are solvable

Titanium dioxide nanoparticles are used in sunscreen to make it transparent instead of white.

Star, February 16, 2009

- *Questions on potential risks were explicitly raised by the media*
- *Link of CNTs and asbestos health*
- *effects on lungs were inferred*
- *Robots replacing humans and getting out of control*
- *Unethical aspects related to nanotechnology were raised*

Web link: http://intraweb.csir.co.za/news/inthenews/2009/TheStar_Nanotech.pdf

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Nanotechnology Risk Concerns in South Africa…

Example 2

Nanotubes may carry asbestos-like health risk

NANOTUBES, one of the wonder materials of the new age of nanotechnology, may carry a health risk similar to that of asbestos, a wonder material of an earlier age that turned into a scourge after decades of use when its fibres were found to cause lung disease, researchers said this week.

This time, the warning comes long before anyone has fallen ill, and experts say the findings call for caution, not alarm, in handling nanotubes, which are tiny, superstrong carbon fibres.

Although nanotubes are already found in some products like tennis racquets, researchers say the fibres appear to pose little risk to consumers.

Nanotubes, discovered in 1991, are essentially rolled-up sheets of carbon that can be used to produce materials that are far lighter and stronger than steel, for example.

But scientists have also long wondered whether the needle-shaped nanotubes might cause the same types of disease as needle-shaped asbestos fibres.

An article published on Tuesday on the website of the journal Nature suggests that the answer may be yes. Researchers said that injecting nanotubes into the abdomens of mice induced lesions similar to those that appear on the outer lining of the lungs after inhalation of asbestos.

In the case of asbestos, lesions eventually be mesothelioma, a deadly ca

Consumers would pro not be able to inhale nano embedded in a golf club cycle frame, for instance.

But there could be a co that nanotubes in pro could be released later, mu asbestos in concrete or mobile brake pads was in by construction workers o chanics.

The greatest risk would people working in laborat or at nanotube manufactu

— © (2008) The New York T

Sunday Times, May 25, 2008

- *CNTs link to health risks similar to asbestos suggested*
- *Current researchers' findings reported in Journal of Nature supports this view*
- *Not yet single case of disease has been reported associated with CNTs*
- *Cautionary approach was proposed*
- *Risk health effects postulated after the products lifespan*
- *Greatest risk for workers in research labs and manufacturing sector were raised*

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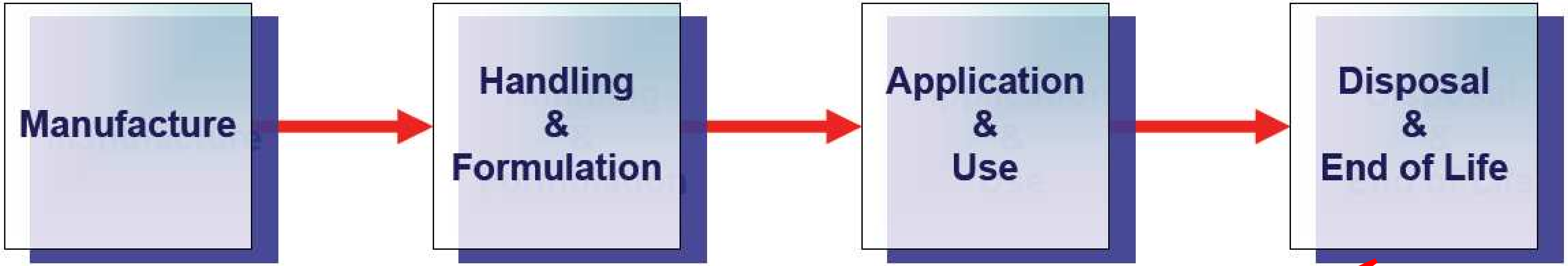
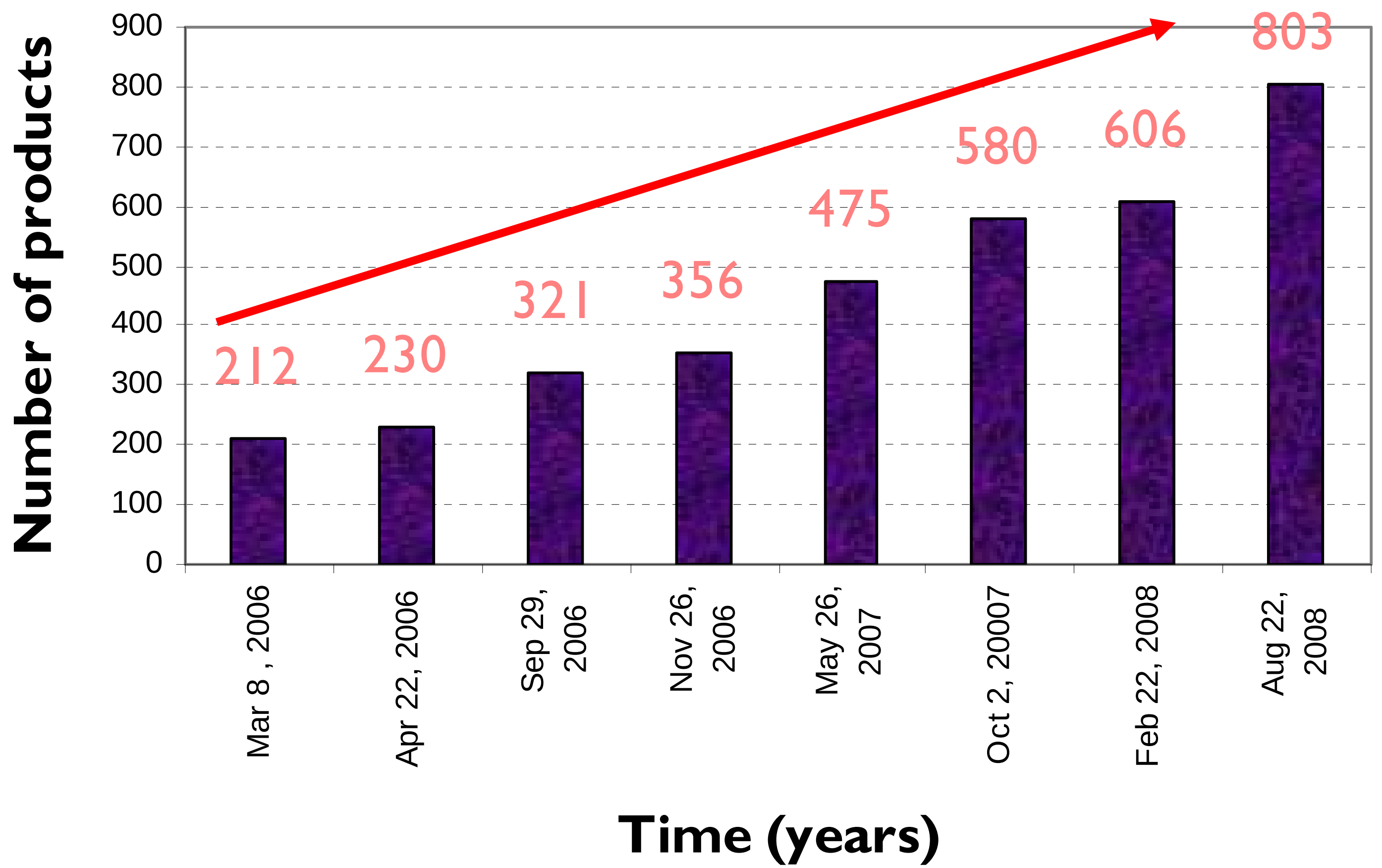
Risk Assessment of NMs in Product Lifecycle



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

Nanoproducts Inventory



Company declared consumer nanoproducts (Woodrow Wilson International Centre for Scholars, March 2009)

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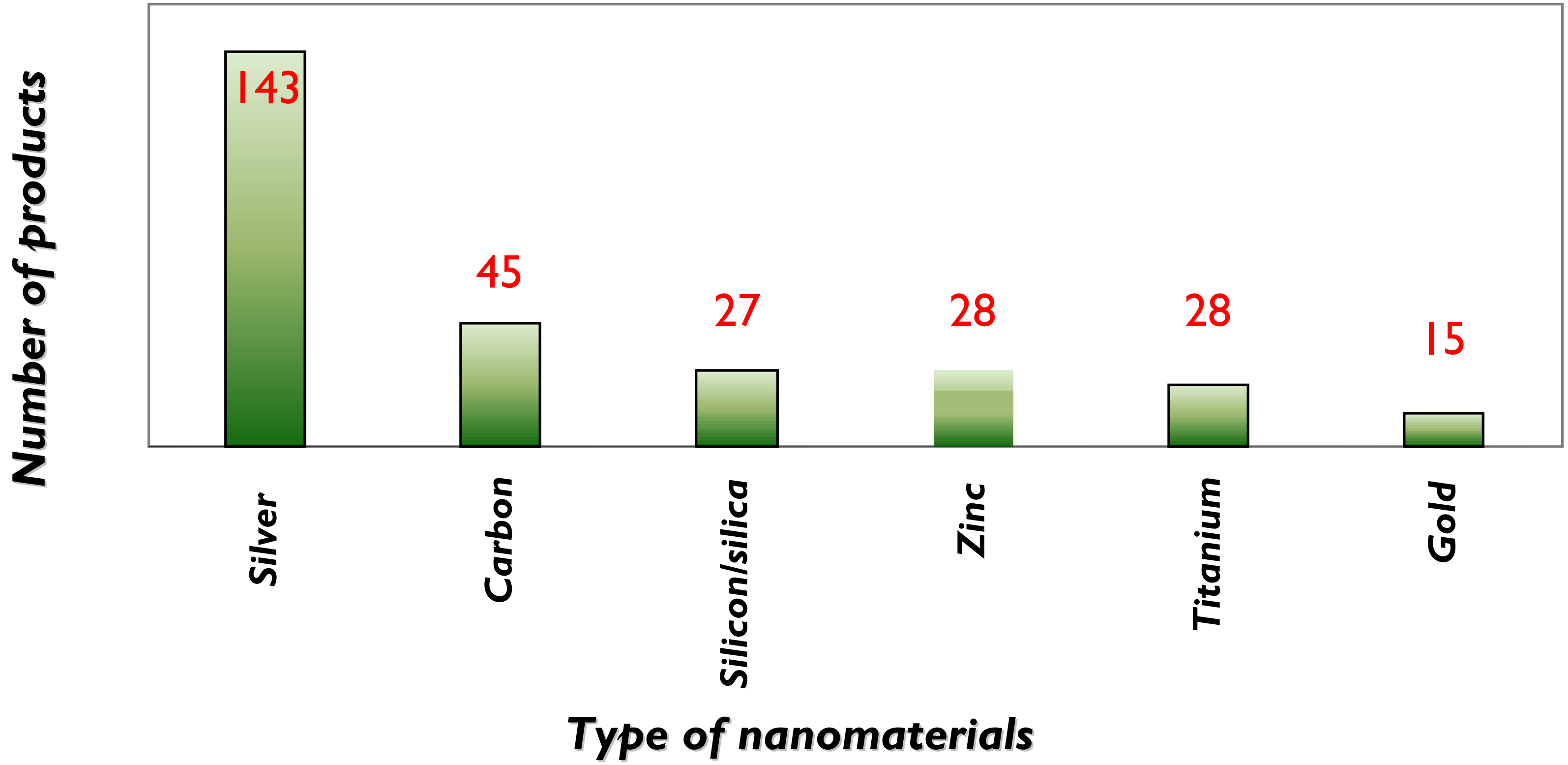
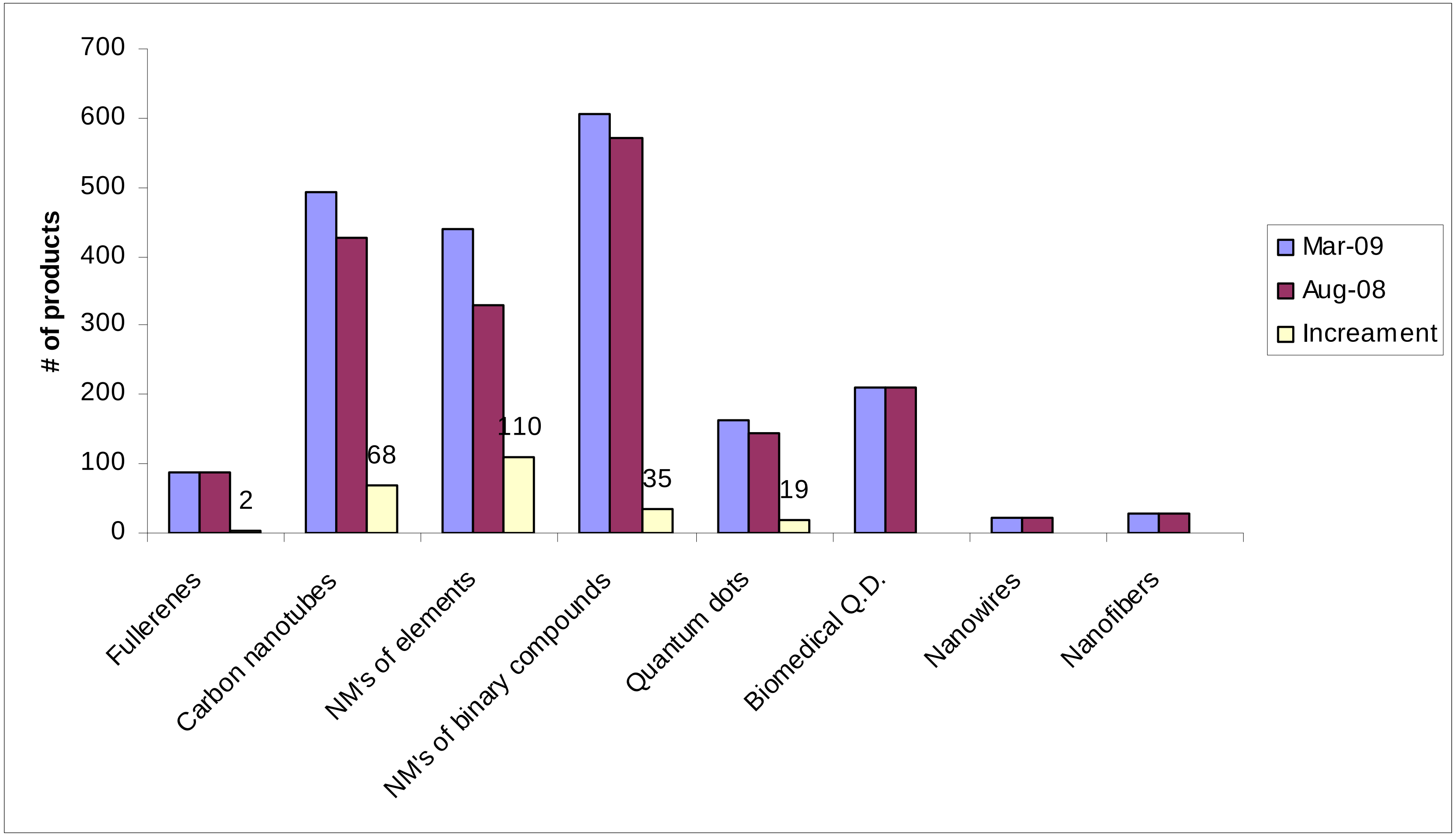
Dominant nanomaterials in nanoproducts



The most dominant nanomaterial(s) in nanoproducts necessitates urgent attention in determining their potential risk to human and environmental health. In South Africa, that is NOT YET KNOWN.

Nanoproducts inventory …(cont..)



Nanoproducts according to the database of Nanowerk Nanomaterial Database (August 2008 (1979) to March 2009 (2213)

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Qualitative Risk Assessment of Nanowastes

- **Risk a function of: hazard (toxicity), 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.

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Qualitative Quantification of NMs Toxicity

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).

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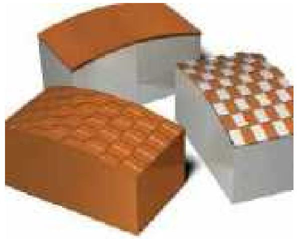
Loci of NMs in Products/Applications

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)

EP: Exposure potential

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Nanowastes Classification

Nanowaste Class	Description	Comments
Class I	• NT: non-toxic • Loci: All loci (low to high exposures)	• May act as Trojan horse/accumulate to high concentrations
Class II	• NT: Harmful to toxic • Loci: Bulk or films (low exposure level) • NMs firmly held in products	• Necessitates to establish chronic effects • Optimal WM approaches should be investigated
Class III	• NT: Toxic to very toxic • Loci: surface or bulk	• Likely to be hazardous, appropriate protocols to be applied
Class IV	• NT: Toxic to very toxic • Loci: suspended solids	• Highly hazardous nanowastes • Efficient and effective technologies yet to be developed • To be disposed off to specialized/designated sites
Class V	NT: very toxic to extremely toxic Loci: free or liquid suspended	• Extremely hazardous waste streams • Efficient and effective technologies yet to be developed • Needs to be handled by specialists • Can cause diverse pollution to diverse ecological systems

Risk Profiles Nanowastes

Application	NMs	Hazard	Exposure potency	Risk at disposal
Sports equipment	SiO_2	Low	Low	Low
	Ag	Medium	Low	Low
	SWCNT	High	Low	Low
	MWCNT	High	Low	Low
Personal care products	Ag	Medium	High	Low
	Fullerenes	High	High	High
	Fe_2O_3	Medium	High	Medium
	TiO_2	Low	High	Low
Food/beverages	TiO_2	Low	Medium	Low
	ZnO	Medium	Medium	Medium
	Fullerenes	High	Medium	High
	Dendrimers	Medium	Medium	Medium
Sunscreen lotions	ZnO	Medium	High	Medium
	TiO_2	Low	High	Low
	Fullerenes	High	High	High
	Dendrimers	Medium	High	Medium

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Quantitative Approach: Computer Model

- Exploit computational power to predict or make estimates – based on best available input data
- Make predictions or estimates of quantities (parameters) characterised by:
  - High costs of measurement
  - Limited technologies for actual environmental measurements
  - Effective initial screening mechanism to elucidate whether actual environmental monitoring is justifiable
  - Provide basis for developing a protocol on best representative data for measurements
  - Explore and create different environmental scenarios that would assist in designing and developing mitigating responses

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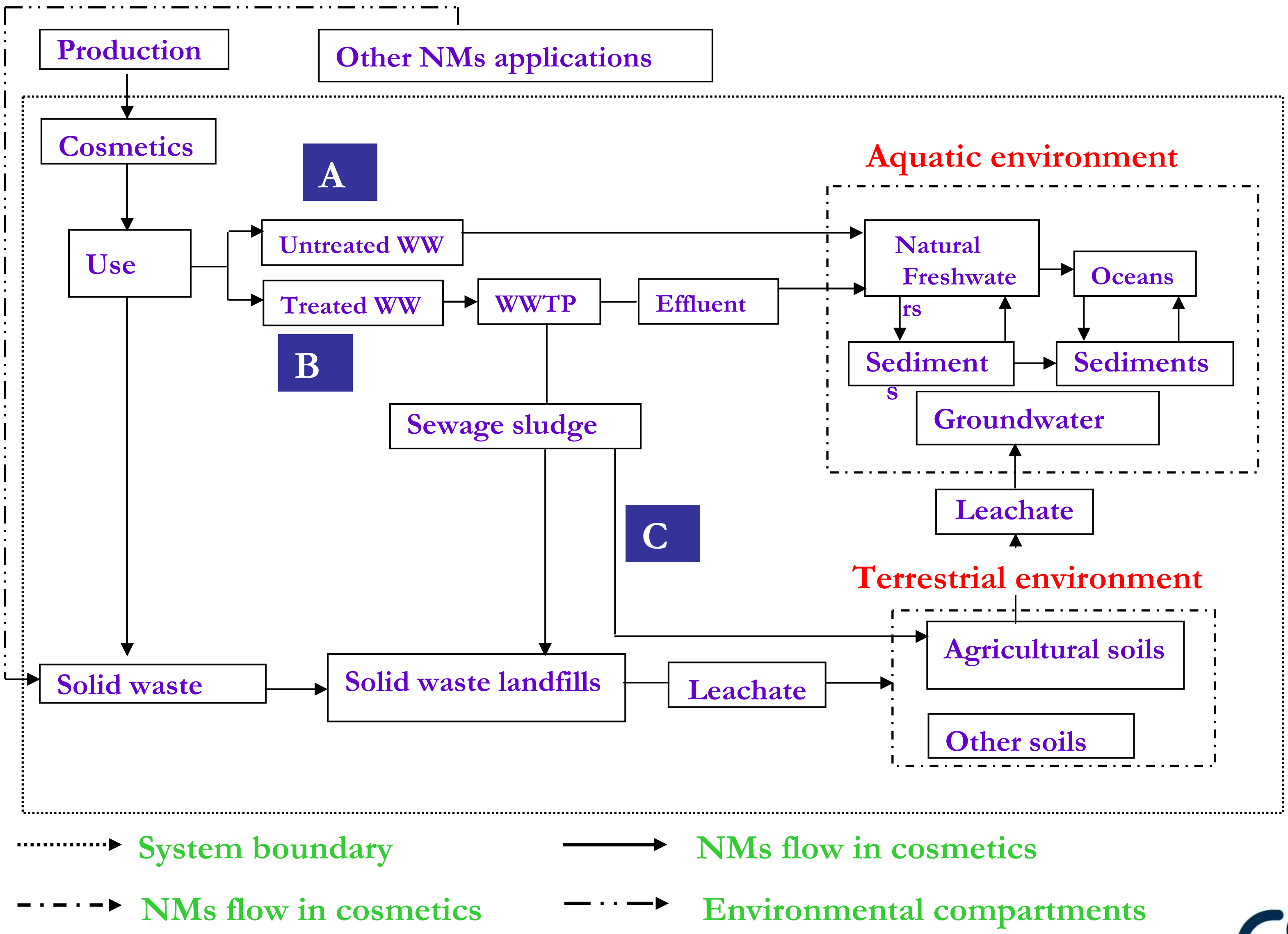
Probable Environmental NMs flows in SA Scenario



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

Cosmetics in SA: Model assumptions

- Use of surrogate data exploited. Switzerland (SW) published data used

- Economic, social, GDP figures used in computation equations to map SW values to SA scenario

- Companies operating in the cosmetic industry are multi-international – likely to market the same form of products in SA as in other parts of the world (concentration of NMs in products constant)

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Map of JHB: Case Study

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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Computed NMs Quantities in JHB (total nAg)

Values in tonnes per annum

Scenarios	GP[1]	Factor[2]	SW	SA	JHB
Minimum	300	0.007	2.100	0.256	**0.038**
Probable	500	0.007	3.500	0.427	**0.085**
Maximum	1230[3]	0.007	8.600	1.050	**0.263**

(Computed nAg quantities in cosmetics: 0.009, 0.021, and 0.063 t/a)

[1] **Global production of nAg in 2007**

[2] **Ration of Switzerland population to major nanotechnology-based countries**

[3] **Values by Muller and Blasser Articles based on scenarios in Switzerland and EU, respectively**

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nAg Distribution in Nanoproducts

Values in tons/annum (t/a)

Nano-based products	**Switzerland**			**South Africa**			**Johannesburg**		
	MIN-E_{SW}	**PRO E_{SW}**	**MAX E_{SW}**	**MIN-E_{SA}**	**PRO-E_{SA}**	**MAX-E_{SA}**	**MIN-E_{JHG}**	**PRO-E_{JHB}**	**MAX-E_{JHB}**
Plastics	0.244	0.407	1.001	0.025	0.128	0.594	0.004	0.026	0.148
Metal products	0.056	0.093	0.228	0.006	0.029	0.135	0.001	0.006	0.034
Cosmetics+	0.506	0.843	2.070	0.052	0.264	1.228	**0.008**	**0.053**	**0.307**
Sprays#	0.360	0.600	1.473	0.037	0.188	0.874	0.006	0.038	0.218
Textiles	0.222	0.371	0.911	0.023	0.116	0.540	0.003	0.023	0.135
Paint/Sealings	0.712	1.187	2.917	0.073	0.372	1.730	0.011	0.074	0.432

+ In addition with supplements

 # In addition to cleaning agents

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Computed NMs Quantities in JHB (total $nTiO_2$)

Values in tons/annum (t/a)

Scenarios	GP	Factor	SW	SA	JHB
Minimum	3000	0.007	21.00	2.153	**0.323**
Probable	5000	0.007	35.00	10.969	**2.193**
Maximum	--	--	400+	236.931	**59.233**

+Schmid, K., and Riedieker, M. Use of Nanoparticles in Swiss Industry: A Targeted Survey, Environ. Sci. Technol. 2008: 42(7); 2253 - 2260

$nTiO_2$ Distribution in Nanoproducts

Values in tons/annum (t/a)

Nano-based products	Switzerland			South Africa			Johannesburg		
	$MIN\text{-}E_{SW}$	$PRO\ E_{SW}$	$MAX\ E_{SW}$	$MIN\text{-}E_{SA}$	$PRO\text{-}E_{SA}$	$MAX\text{-}E_{SA}$	$MIN\text{-}E_{JHG}$	$PRO\text{-}E_{JHB}$	$MAX\text{-}E_{JHB}$
Plastics	0.43	0.71	8.13	0.04	0.22	4.82	0.007	0.05	1.20
Metal Products	12.33	20.54	234.80	1.264	6.44	139.10	0.19	1.29	34.77
Cosmetics+	0.46	0.76	8.71	0.05	0.24	5.158	**0.007**	**0.048**	**1.289**
Sprays#	2.57	4.28	48.95	0.26	1.34	28.99	0.04	0.27	7.25
Textiles	0.08	0.13	1.52	0.008	0.04	0.90	0.001	0.008	0.225
Paint/Sealings	5.140	8.567	97.906	0.527	2.684	57.993	0.079	0.537	14.498

+ In addition with supplements

In addition to cleaning agents

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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**

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

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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JHB WWTP (High Efficient Plants)

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

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JHB WWTP (High Efficient Plants)… cont…

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

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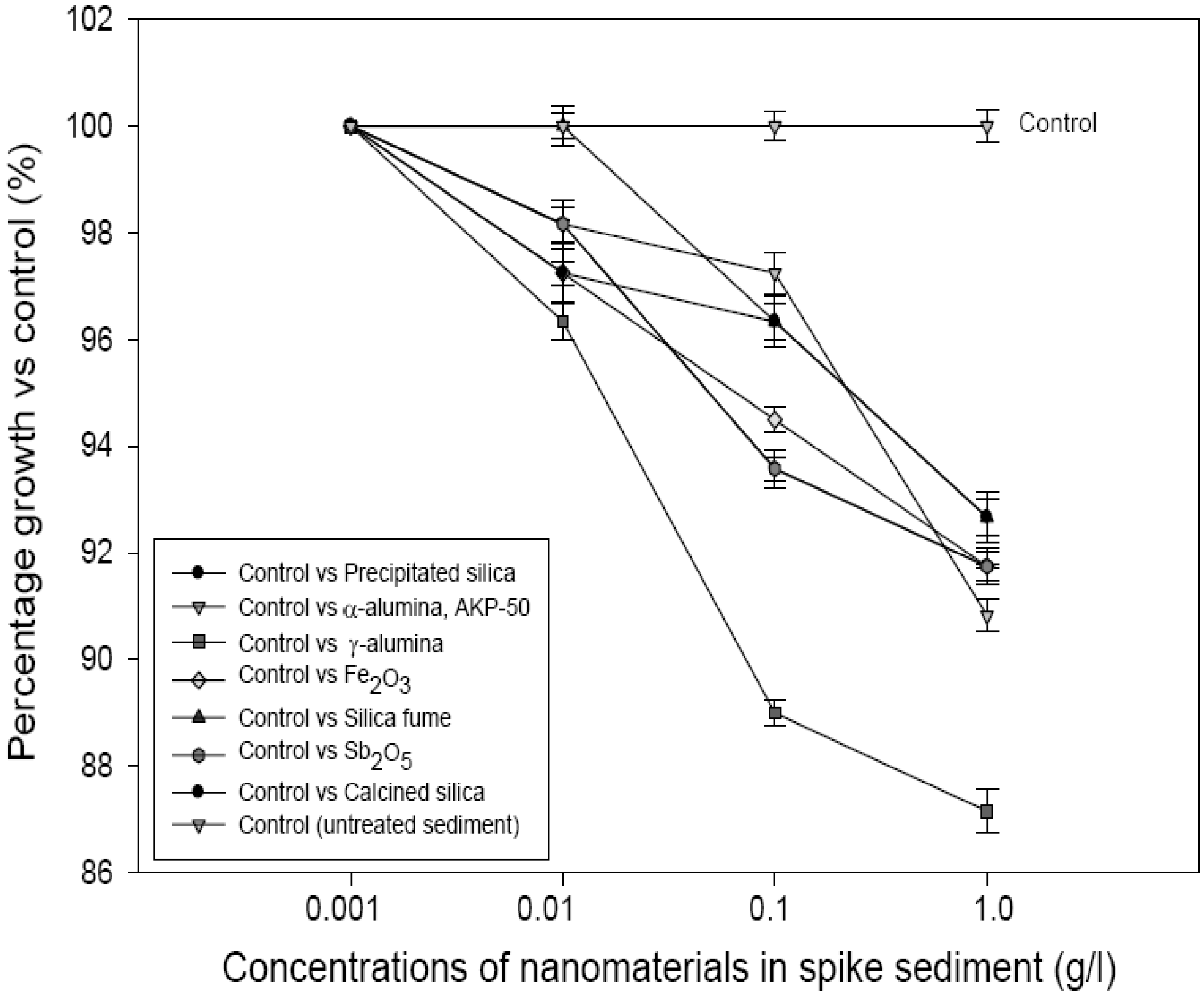
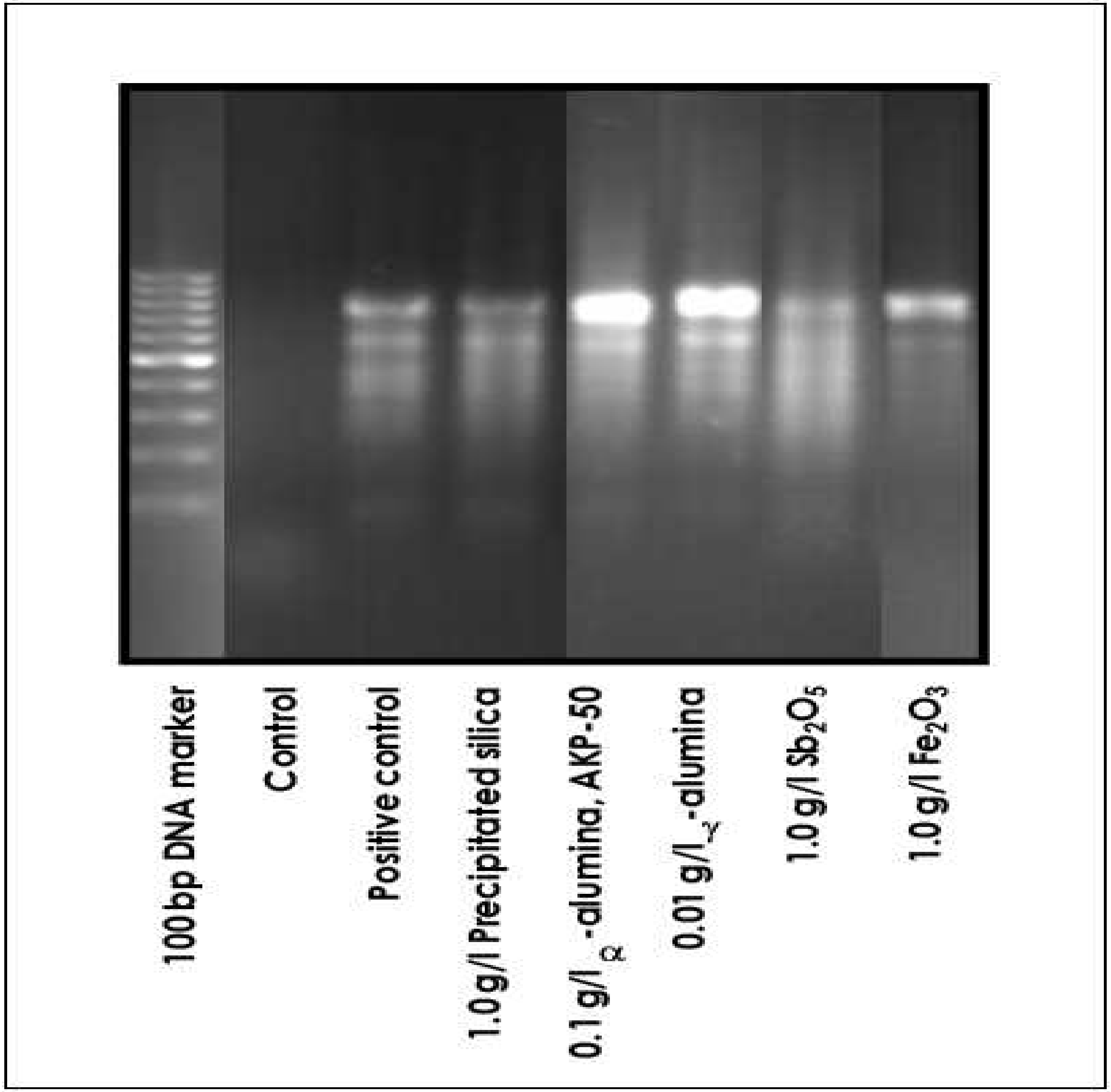
Growth Inhibition



NMs Effects on DNA



DNA fragmentation

Quantitative Model 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

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JHB WWTP (Low Efficient Plants)… cont…

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**

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Quantitative Model Results (Lower Eff)

	Parameters	MIN-E_{JHG}		PRO-E_{JHB}		MAX-E_{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

- Qualitative and quantitative models used in quantifying risks of NMs in the environment – based on current scientific data
- Presently, high degrees of uncertainty noted in the data used in the model
- Quantities released into environment driver for the risks levels ($nTiO_2$ > nAg) – yet nAg more toxic than $nTiO_2$
- Ecotoxicological data for tropical organisms needed (presently lacking) – this limits the models replica to actual environmental conditions in JHB
- Necessity for inventory of NMs and nanoproducts in developing countries such as SA to ascertain levels of risks

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